MONITORING OF COLLEGE LABORATORY EMISSIONS FOR TRACE METAL CONTAMINATION

Thesis

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MONITORING OF COLLEGE LABORATORY EMISSIONS FOR TRACE METAL CONTAMINATION

by

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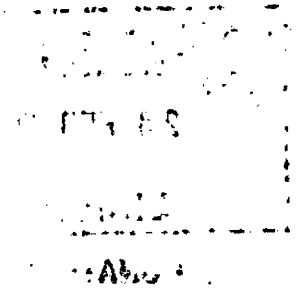

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DECLARATION

I hereby declare that the substance of this thesis has not been submitted, nor is being concurrently submitted, in candidature for any other degree.

I also declare that the work embodied in this thesis is the result of my own independent investigation. Where the work of others has been used, this has been fully acknowledged in the text.

R L Nurton

Professor G Coleman
Director of Studies

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DEDICATED TO MY MOTHER
LINDA MAY NURTON

CONTENTS

ABSTRACT

A general review of urban air pollution including regulations and guidelines, meteorological effects and monitoring of urban air quality, precedes a more detailed study of trace metals in the atmosphere. This study covers sources of trace metal pollution, harmful effects of high metal levels in the atmosphere and details of long-term surveys carried out by other air monitoring laboratories.

Air monitoring equipment was set up on the roof of the Science Block at the Llandaff site of CIHE to sample air emissions from laboratory fume cupboard ducting that ventilated from student chemical laboratories contained in the building. Particulate collection was achieved by capture on filters using high volume pumps for periods of time ranging from 24 hours to 2 weeks.

Analyses of the particulates collected for trace metal contamination were undertaken using atomic absorption spectrometry. This method required acid digestion of the filter and particulates combined, and the resultant solution analysed using specific element cathode lamps. The results obtained were compared with the quality standards or guidelines set out by EC directives and other relevant authorities. Methodology of sampling was adjusted accordingly to ensure its representation and accuracy of emissions from the laboratories.

This primary investigation posed various questions and suggested new directions for future projects. Recommendations are drawn from the results and subsequent discussion.

CHAPTER ONE

INTRODUCTION

1.1 A Background to Urban Air Pollution

Most people either live in cities and towns or regularly use them for work, education, business and a range of other activities. Indicators have shown that the quality of life in urban areas has greatly improved with respect to health and well being. One of the main indicators is the improvement in air quality.

Since the post-war years, urban "pea-souper" smogs have become less common. Almost certainly this can be attributed to the Clean Air Acts of 1956 *[1]* and 1968 *[2]* which resulted in smoke control areas being set up and thus cleaning up pollution such as domestic coal burning.

As this problem has receded, public attention has switched to other wider scale pollution issues such as acid rain, ground level ozone, stratospheric ozone depletion and global warming. Whereas huge resources have been devoted to these issues, contemporary urban air quality has not received the same commitment from researchers.

However, an Environment White Paper : "This Common Inheritance" *[3]* reflected a growing interest in the urban environment by promising increased air quality monitoring for pollutants in our cities. Furthermore, it provided wider dissemination of air quality data to the general public together with relevant health advice. Considerable detail has been added to urban air quality policy in two annual reports *[4, 5]* further to the original Environment White Paper.

The Department of the Environment has formed the Quality of Urban Air Review Group from independent expert scientists, whose first report in 1993 *[6]* puts urban air quality problems into context and suggests a research and monitoring strategy covering a period up to 1995.

1.2 Issues Relating to Urban Air Quality

Foremost, the general public want to know whether or not urban air is a risk to health. There is no straightforward answer to that and much more information is required.

In terms of air quality and health, many pollutants give cause for concern including :

- oxides of nitrogen
- sulphur compounds
- carbon monoxide
- particulate matter
- oxidants
- trace metals
- organic compounds

After human health, the Urban Air Review Group suggest that the next most important issue to the population concerns dirt, grit and urban soiling. Urban areas are increasingly becoming congested with motor traffic. Smoke from diesel vehicles has taken over from coal smoke as the major cause of blackening of building surfaces. Coal burning in homes and industrial boilers

and furnaces together with industrial activities, lead to grit and dust problems and the associated trace element contamination of soils and building surfaces.

Some pollutants are emitted directly into the atmosphere and are known as primary pollutants. Others are formed in the air as a result of chemical reactions with other pollutants and atmospheric gases, and are known as secondary pollutants. Carbon monoxide and sulphur dioxide are examples of primary pollutants, while ozone is a secondary pollutant. Some pollutants, such as nitrogen dioxide can be both a primary and a secondary pollutant i.e. some nitrogen dioxide is emitted into the atmosphere from power stations and vehicle exhausts, and some is formed from the oxidation of nitric oxide in the air.

Distinction between these pollutants is important for understanding urban air pollution and divising appropriate control strategies. For primary pollutants there is likely to be a proportional relationship between emissions and ambient concentrations. However, with a secondary pollutant, reducing emissions of its precursors may not lead to a proportional reduction in its ambient concentration, and in some circumstances may actually lead to an increase in concentrations.

1.3 Emission Regulations

There are a number of pollution abatement methods available to Governments. These include voluntary agreements between Industry and the State; fiscal incentives to encourage consumers to buy less polluting products; and regulation. In recent years the latter has been the most widely used control instrument.

For many years the application of "best practicable means" (BPM) to prevent or minimise emissions from industrial processes was the basis of pollution control. This was replaced in 1990 by the concept of "best available techniques not entailing excessive costs" (BATNEEC) *[7]*. This approach assumes that technology is the only means of reducing emissions. Recently the Government has moved towards an effects-based approach to air pollution in which pollution abatement policy is determined within the context of air quality standards and other environmental criteria.

1.4 Air Quality Criteria

When discussing urban air quality it is useful to compare ambient concentrations with internationally agreed air quality criteria. These criteria are based primarily on assessments of the human health effects of single pollutants. However, most of the major urban air pollutants also have adverse effects on plants and several air quality criteria have been adopted to protect vegetation. When considering criteria set by the European Union (EU), it is important to distinguish between air quality limit values and air quality guide values. Limit values are mandatory, whereas guide values are designed to provide guidance. Air quality standards can contain both limit and guide values. Guidelines, as distinct from standards, have been proposed by other bodies such as the World Health Organisation (WHO) *[8]*.

Individual response to a given concentration of air pollution varies considerably. For example, individuals with pre-existing lung disease may be more sensitive to a given dose of pollution than healthy people. Differences in response can also be due to age, sex and the level of exercise taken. Air quality criteria generally aim to minimise the ill-health impact on sensitive groups of

people. Protection factors have been applied by the WHO to take account of current scientific and medical uncertainties.

Effects of pollution on human health depend on duration of exposure as well as pollutant concentration. Thus, there are different air quality guidelines/standards and averaging times for both long term (chronic) exposure and short term (acute) exposure. Some pollutants have both chronic and acute effects and for these criteria are set for both short and long term averaging periods.

One of the major shortcomings of the currently accepted air quality criteria is that pollutants are generally considered in isolation from each other rather than in combination. This is because little is known of the effects of mixtures of pollutants and therefore insufficient information to enable the setting of such criteria.

An approach sometimes accepted for setting ambient air quality criteria is to divide occupational exposure standards by 40 to take account of potential sensitivity to air pollution of certain groups of the non-working population such as young children and the elderly, and their possible longer exposure time compared to that of the workplace *[9]*.

1.5 Meteorological Influences

Pollution concentrations vary considerably from hour to hour and from one day to another. These variations are largely determined by meteorological factors. These concentration variations are caused by wind speed, turbulence, mixing depth and urban topography. To a first approximation, concentrations are

inversely proportional to wind speed for ground level sources, while atmospheric turbulence determines how rapidly a parcel of polluted air is dispersed away from a given source. This dispersion is less under stable atmospheric conditions which occur largely at night-time, as heating of the ground during the middle of the day causes thermal turbulence.

The greater surface roughness encountered in urban areas, due to varying building heights, generally acts to increase turbulence and enhance dispersion. The exception is during periods of very light winds when stagnation of air recurs close to the ground. The principal effect of increased turbulence in urban areas is to reduce ground level concentrations, but where elevated point sources such as chimney stacks occur, increased turbulence brings smoke plumes down to the ground more rapidly resulting in higher concentrations.

1.6 Monitoring of Urban Air Quality

Air quality monitoring has a distinct role to play in air quality management, particularly in urban areas. The air quality in a particular location is not simply due to events and circumstances which are without control. Much of the air pollution present at a particular location is likely to be a consequence of sources quite close by. Air quality can be a function of human activities, which themselves could be modified or managed in such a way as to reduce levels of certain pollutants. Broadly speaking, the aim of monitoring is to set up a system of observation and to collect enough data to test predicted patterns of dispersion. This should enable any environmental problem to be discovered and explained, and a remedy sought.

1.7 Air Monitoring Techniques

There are basically two types of air quality monitoring equipment. Firstly, there are continuous automatic monitors using sophisticated electronic techniques to give more or less instantaneous measurements of air pollution concentrations. These allow peak concentrations to be highlighted and the data can readily be downloaded to a control computer.

Secondly, there are relatively simple techniques which are less sensitive, having longer averaging times. These times are typically 24 hours to one month, making data acquisition and dissemination more difficult. In general, automatic analysers have exacting requirements in terms of power supply, stable air temperature and protective housing. They normally require regular visits and calibration by trained operatives.

The second approach involves the use of less automated techniques such as wet chemical methods for measuring air pollution. Whilst these methods are intended to be specific to one pollutant, they can suffer interferences from other chemicals in the air. For example, the potassium iodide oxidant method measures all the oxidants in the air including ozone and nitrogen dioxide, and these results can prove to be unreliable due to interference if sulphur dioxide is present.

In recent years, passive diffusion tubes that are specific to one pollutant have been developed. An example is the measurement of nitrogen dioxide at ambient levels. They are cheap and easy to use, needing no power supply or protective housing. However, the accuracy of diffusion tubes has recently been questioned, as they may be affected by wind in exposed locations. Despite their limitations, they provide a cheap and convenient way of identifying the

spatial distribution of pollution, highlighting hotspots and identifying trends in average concentrations.

The siting of an air monitoring station is critical, or concentrations of pollutants can vary widely over an urban area. The purpose of the monitoring will decide the actual siting of the station, e.g. compliance with EC air quality directives may require different sitings than those of researchers looking to enhance knowledge of atmospheric chemistry.

1.8 Objectives of this Study

In the late 1980's, a curriculum greening movement began with the aim of encouraging Colleges to recognise practically their environmental responsibilities. They needed to introduce measures to successfully audit their campus buildings for compliance with a standard such as BS7750 *[10]*, an environmental management system. This audit should lead to the adoption of a comprehensive environmental policy statement with an action plan for its implementation.

BS7750 entails a structured approach to management of the environmental effects of an organisation. Three essential criteria need to be satisfied for implementing this standard.

1. The determination of significant environmental effects;
2. The identification of regulatory requirements and other guidelines;
3. The development and implementation of procedures for compliance and assurance testing by environmental auditing.

It was the wish of the School of Environmental Sciences of Cardiff Institute of Higher Education (Llandaff) to undertake a series of projects to evaluate and quantify any significant environmental burdens produced by the Institute. These projects hopefully will form the basis of an environmental auditing programme to be undertaken by CIHE.

The objective of this particular project was to purchase suitable equipment to enable a portable air monitoring system to be set up and fully tested. This system needed to successfully collect particulate matter from a measured volume of air and allow subsequent analysis of the collected particulates for pollutants.

Being portable, this equipment could be used on-site as part of the auditing programme mentioned above, or transported off-site by students wishing to undertake similar air monitoring projects in suspected problem areas.

CHAPTER TWO

TRACE METALS IN THE ATMOSPHERE

2.1 Introduction

Trace metal pollutants are emitted into the atmosphere from numerous sources. These include combustion of fossil fuels (including leaded petrol), metal smelters and alloy refineries, cement manufacturing plants and municipal incinerators *[11]*.

Metals and metallic compounds exist in the atmosphere in three distinct physical forms; solid particulate matter, liquid droplets (mists) and vapours. The size range of airborne particulate matter is broad and particles represent by far the most common form of metallic air pollution. The levels of metals in suspended particulate matter as measured by the US National Air Sampling Network *[12]* is shown in Table 2.1. Figures such as these give an indication of levels likely to be encountered during ambient air monitoring and may thus be used to estimate the volume of air which needs to be sampled to allow collection of a quantity of a metal which is compatible with a proposed analytical technique.

TABLE 2.1 AVERAGE AND MAXIMUM CONCENTRATION OF AIRBORNE POLLUTANTS MEASURED AT URBAN STATIONS BY THE US NATIONAL AIR SAMPLING NETWORK 1964-65 *[12]*

POLLUTANT	CONCENTRATION ($\mu g\ m^{-3}$)[a] Arithmetic Average	MAXIMUM
Total suspended particulate matter	105	1254
Antimony (Sb)	0.001	0.160
Arsenic (As)	0.02	
Beryllium (Be)	<0.0005	0.010
Bismuth (Bi)	<0.0005	0.064
Cadmium (Cd)	0.002	0.420
Chromium (Cr)	0.015	0.330
Cobalt (Co)	0.0005	0.060
Copper (Cu)	0.09	10.00
Iron (Fe)	1.58	22.00
Lead (Pb)	0.79	8.60
Manganese (Mn)	0.10	9.98
Molybdenum (Mo)	<0.005	0.78
Nickel (Ni)	0.034	0.460
Tin (Sn)	0.02	0.50
Titanium (Ti)	0.04	1.10
Vanadium (V)	0.05	2.20
Zinc (Zn)	0.67	58.00

a - Bi-weekly 24-hour samples.

2.2 Sources of Trace Metal Pollution

Metals occur in the atmosphere mainly in particulate form originating from the mixing of finely divided materials from various sources. Both natural and anthropogenic sources contribute to atmospheric trace metal loads. The relative strength of each contribution varies from metal to metal as well as spatially and temporally. Natural sources mainly comprise wind blown material, volcanogenic emissions, sea salt aerosols and vegetation combustion products. The principal anthropogenic sources are fossil fuel combustion, ferrous and non-ferrous metallurgical industries, vehicle emissions, waste incineration and the cement and fertiliser industries.

When discussing sources some other points are worth making :

- natural trace metal sources tend to act as "area sources" while anthropogenic sources tend to act more as "point sources".
- re-suspension of deposited material to the atmosphere readily takes place in the urban environment due to such features as paved surfaces.

In the major anthropogenic sources, materials are volatilised at high temperature and re-condense on particulate matter before emission to the atmosphere. The exception is mercury which for the most part is emitted as a vapour and remains in the atmosphere. The form of metals in particulate matter is varied and sometimes complex. They may occur as elemental metal, in inorganic form such as oxides and chlorides and in organic form such as methyl compounds. They are also present in different valency states with corresponding different reactivity and toxicity. In many cases concentrations are at the limits of detection and most methods of particulate analysis measure only the metal concentration and do not differentiate between the forms in

which the metals are present. Consequently, our understanding of the speciation of metals in the atmosphere is incomplete.

A key feature of trace metal behaviour in atmospheric particles is the variation in concentrations with particle size. For metals of pollutant interest this behaviour is intrinsically related to their generation. Volatile materials, especially those (such as cadmium, lead and zinc) which form oxides are vaporised during high temperature combustion processes *[13]*. The volatile metals then condense onto the surfaces of ambient particles. This process is generally size dependent since smaller particle condensation nuclei have a larger surface area/volume ratio. Two important points follow from this behaviour.

- It is generally the smaller particles produced during high temperature combustion processes which are most likely to pass through emission controls and escape to the atmosphere, their small size allowing maximum transport from the source.
- Trace metals are readily absorbed by biological systems, be it through contact with living tissues or dissolved in water supplies *[14]*.

Estimates of atmospheric emissions in the UK have been analysed by Warren Spring Laboratory *[15]*. They use data published by Pacyna *[16]*, Pacyna and Munch *[17]*, Hutton and Symon *[18]*, and the UK submission to the Secretariat of the Working Group or the Atmospheric Input of Pollutants to the North Sea (ATMOS 1990) *[19]*. Data from the Coleman analysis are summarised in Table 2.2, which has been compiled by taking the mean of the values available in the three inventories.

Emissions of **arsenic** are mainly from the combustion of fuels and the smelting of metals, particularly in the production of copper and nickel. In air it is present mainly as inorganic arsenic in particulate form.

Beryllium, cobalt, molybdenum and **antimony** arise predominantly from the combustion of coal and **vanadium** from the burning of residual and fuel oils.

Nickel also arises mainly from the burning of coal and oil and occurs principally as soluble nickel sulphate in fly ash, though some is in the form of insoluble oxides. The largest single source of **cadmium** is the smelting of non-ferrous metals, principally copper, nickel and zinc. Fossil fuel combustion also produces a significant proportion as also does waste incineration. A smaller proportion arises from the production of iron and steel. **Chromium** and **manganese** enter the atmosphere mainly from processes involved in the production of iron and steel with a smaller proportion from the combustion of fossil fuels, mainly coal.

Copper and **zinc** come mainly from smelting processes with smaller but not insignificant emissions arising from the burning of fossil fuels. Tyre wear is also a source of zinc.

The dominant source of **lead** is petrol combustion. In January 1986 the permitted lead content of petrol was reduced from 0.40 to 0.15 g l^{-1} and there has been the subsequent introduction of lead-free petrol. As a result lead emissions have reduced substantially.

Production of ferrous and non-ferrous metals, fossil fuel combustion and waste incineration all produce a significant proportion of the present total of lead emission.

TABLE 2.2 UK EMISSIONS OF HEAVY METALS (Ref. Years 1979, 82, 83) IN TONNES/ANNUM *[15]*

	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	TOTAL
Non ferrous metals	82	19	-	147	630	2	10	1620	2510
Fossil fuel combustion	130	12	222	246	150	16	864	230	1870
Iron/steel production	9	4	870	97	490	2	19	480	1971
Cement production	8	1	26	-	30	3	-	140	208
Waste incineration	1	11	16	88	170	5	2	970	1263
Petrol Consumption	-	-	-	-	6800	-	-	-	6800
Chlor-alkali production	-	-	-	-	-	9	-	-	9
Miscellaneous	9	0.5	-	2	12	0.5	2	2	28
TOTAL	239	47.5	1134	580	8772	37.5	897	3442	14659

2.3 Harmful Effects from Trace Metals in the Atmosphere

The human body and other biological systems have a tremendous capacity to take in all types of compounds, and either utilise them to support some bodily function or eliminate them. Some of these chemicals enter the body by inhalation.

The concept of total body burden refers to the way a trace material accumulates in the human system. The components of the body that can store these materials are the blood, urine, soft tissue, hair, teeth and bone. The blood and urine allow more rapid removal of trace materials than the soft tissue, hair and bone *[20]*. Accumulation results when trace materials are stored more rapidly than they can be eliminated. It can be reversed when the source of the material is reduced. The body may eliminate the trace material over a period of a few hours to days, or may take much longer - often years.

The impact of air pollution on human beings has been the major force motivating efforts to control it. Most persons do not have the luxury of choosing the air they breathe. Working adults can make some choices in the selection of their occupation and the place where they live and work, but children and the non-working elderly often cannot.

Air pollution principally affects the respiratory, circulatory and olfactory systems. The respiratory system is the principal route of entry for air pollutants, some of which may alter the function of the lungs.

Lead, by far the largest pollutant, is particularly hazardous to young children. It can degrade renal function, impair haemoglobin synthesis and alter the nervous system. There are two routes for the entry of lead - inhalation and

ingestion. Inhalation results in primary exposure to airborne lead, whereas ingestion may result in secondary exposure via contamination of the ingested material by atmospheric lead. When lead is inhaled, some of it is absorbed directly into the bloodstream and a fraction into the gastrointestinal tract via lung clearance mechanisms that result in the swallowing of unueus.

Other metals in the environment of potential hazard to man are cadmium which may influence hypertension and emphysema, nickel as the carbonyl which is carcinogenic, antimony which is toxic, beryllium which can cause berylliosis and methyl mercury which is highly toxic. At present levels of exposure, lead, cadmium and possibly nickel are potentially hazardous to health. Only under special circumstances and in special compounds are a few other elements hazardous.

2.4 Review of Previous Atmospheric Trace Metal Measurements in Urban Areas

There are several sources of information on metals in the atmosphere in both urban and rural areas. These sources comprise the following :

- long term measurements of a range of metals by Warren Spring Laboratory and AEA Technology, Harwell;
- metal specific studies (eg Hg and Pb) at various sites by Warren Spring Laboratory;
- various ad hoc studies by local authorities, government agencies, research establishments and industry.

The first and second categories give the best overall picture especially as regards temporal trends. The latter type of study is still useful, however, especially as they can focus on "hot spots" where exceedence of guidelines and standards could potentially occur. Warren Spring Laboratory operate the Multi-element Survey on behalf of the Department of the Environment. The programme began in 1976 with measurements at 20 monitoring sites in a range of UK urban locations. After 2 years the programme was reduced to cover 5 stations which had produced relatively high concentrations of the 15 elements monitored during the first 2 years. The objective of the Multi-element Survey is to provide data on concentrations and trends of a range of trace elements at the 5 urban locations. The outputs of the Warren Spring Laboratory measurement programme comprise a series of Summary Reports for each year's results. A recent report *[21]* analyses trends between 1976-77 and 1988-89 and results are shown in Table 2.3.

As a part of their survey of atmospheric trace elements in the UK, AEA Technology, Harwell, have maintained monitoring stations at several UK locations for a number of years from the mid 1970's to 1989. Outputs of those measurement programmes are produced in annually published reports of a year's summarised data *[22, 23]*.

Numerous ad hoc studies of atmospheric trace metals have been carried out in recent years. Typically, these have focused on a specific industry or area to assess its contribution to ambient concentrations of atmospheric trace metals.

TABLE 2.3 **WSL MULTI-ELEMENT SURVEY ANNUAL AVERAGE CONCENTRATIONS (ng m^{-3}). APRIL 1976 - MARCH 1989** *[21]*

Element	76-77	77-78	78-79	79-80	80-81	81-82	82-83	83-84	84-85	85-86	86-87	87-88	88-89
Arsenic	6.5	7.1	6.1	-	-	7.0	12	-	-	-	-	-	-
Beryllium	0.30	0.25	0.25	-	-	0.34	0.24	-	-	-	-	-	-
Cadmium	7.1	4.9	4.4	4.5	2.7	2.5	1.7	2.8	2.6	2.4	1.5	3.2	3.5
Cobalt	1.8	1.9	1.3	-	-	1.5	1.2	-	-	-	-	-	-
Chromium	18	19	9.5	-	-	16	12	16	5.6	6.4	7.8	7.1	6.9
Copper	54	42	38	28	26	23	21	20	22	24	47	35	18
Iron	1670	1420	1070	1000	1000	1000	960	990	790	930	830	860	920
Manganese	64	58	40	29	26	30	28	33	29	29	26	28	24
Molybdenum	4.6	3.4	3.2	-	-	3.1	1.9	-	-	-	-	-	-
Nickel	22	22	20	-	-	14	12	12	12	12	8.9	11	14
Lead	820	610	650	620	480	500	430	380	370	350	220	200	190
Antimony	9.0	9.7	8.9	-	-	5.9	4.0	-	-	-	-	-	-
Titanium	74	62	68	-	-	20	15	-	-	-	-	-	-
Vanadium	50	33	48	22	20	24	23	19	32	14	14	14	10
Zinc	860	820	440	270	200	200	120	110	100	130	120	160	170

2.5 Air Quality Standards and Guidelines for Trace Metals

The primary aim of the air quality guidelines is to provide a basis for protecting public health from adverse effects of air pollution and for eliminating or reducing to a minimum, those contaminants of air that are known or likely to be hazardous to human health and well-being.

These guidelines are intended to provide background information and guidance to governments in making risk management decisions, particularly in setting standards, but their use is not restricted to this. They also provide information for all who deal with air pollution.

It should be emphasised that when air quality guidelines are given, these values are not standards in themselves. Before standards are adopted, the guideline values must be considered in the context of prevailing exposure levels and environmental, social, economic and cultural conditions. In certain circumstances there may be valid reason to pursue policies which will result in pollutant concentrations either above or below the guideline values. Air quality standards and guidelines for a series of metals are given in Table 2.4. The only metal for which there is EC air quality legislation is lead with a limit value of 2$\mu g\ m^{-3}$ as an annual average. The US EPA ambient air quality standard for lead is 1.5 $\mu g\ m^{-3}$ as a quarterly average. There are WHO air quality guidelines for cadmium, magnesium, lead and vanadium. In addition, using the criteria of the International Agency for Research on Cancer (IARC), WHO have identified arsenic, chromium and nickel as being carcinogenic and give no safe threshold for atmospheric concentrations. The Health and Safety Executive (HSE) quote long term Occupational Exposure Limits (OEL) for each metal listed. An OEL is based on exposure for 8 hours per day, 5 days per week. The HSE OEL values are sometimes, for example by Her Majesty's

Inspectorate of Pollution (HMIP), reduced by a factor of 40 to allow for exposures in excess of a working week and for elderly or ill persons being exposed.

It is worth noting that although most metals are not covered by legislation as regards their atmospheric concentrations, emissions of such metals (eg. Cr, Mn, Cu, Ni, As, Sn, Cd, Sb, V, Co and Hg) from certain types of industrial and commercial sources are regulated by HMIP and local authorities.

TABLE 2.4 EC LIMIT, WHO GUIDELINES and HSE OCCUPATIONAL EXPOSURE LIMITS ($\mu g\ m^{-3}$) FOR HEAVY METALS

METAL	EC LIMIT	WHO GUIDELINE	OEL/40
Arsenic (As)	-	nsl	2.5
Beryllium (Be)	-	-	0.05
Cadmium (Cd)	-	0.001-0.005 rural 0.01-0.02 urban	1.25
Cobalt (Co)	-	-	2.5
Chromium (Cr)	-	nsl*	1.25
Copper (Cu)	-	-	5
Manganese (Mn)	-	1	25
Nickel (Ni)	-	nsl	2.5
Lead (Pb)	2	0.5-1.0	3.75
Iron (Fe)	-	-	25
Antimony (Sb)	-	-	12.5
Titanium (Ti)	-	-	135
Vanadium (V)	-	1 (24-hour av)	1.24
Zinc (Zn)	-	-	25
Tin (Sn)	-	1	50
Mercury (Hg)	-	-	1.25

CHAPTER THREE

METHODOLOGY FOR AIR SAMPLING AND COLLECTION

3.1 Fundamental Requirements of a Sampling System

The principal requirement of a sampling system is to obtain a sample that is representative of the atmosphere at a particular place and time, and this can be evaluated as a mass or volume concentration. The sampling system should not alter the chemical or physical characteristics of the sample in an undesirable manner. The major components of most sampling systems are an inlet manifold, an air mover, a collection medium, and a flow measurement device. The inlet manifold transports material from the ambient atmosphere to the collection medium or analytical device, preferably in an unaltered condition. Inlet manifolds are made out of glass, Teflon, stainless steel, or other inert materials and permit the remaining components of the system to be located at a distance from the sample manifold inlet.

The air mover provides the force to create a vacuum or lower pressure at the end of the sampling system. In most instances, air movers are pumps.

The collection medium for a sampling system may be a liquid or solid sorbent for dissolving gases, a filter surface for collecting particles, or a chamber to contain an aliquot of air for analysis.

The flow device measures the volume of air associated with the sampling system. Examples of flow devices are mass flow meters, rota meters and critical orifices.

Sampling systems can take several forms and may not necessarily have all four components. The system devised for this work consists of "open-face" filter collection, in which the filter is directly exposed to the atmosphere being sampled. Obviously this excludes the use of an inlet manifold for this particular system.

Regardless of the configuration or the specific material sampled, several characteristics are important for all ambient air sampling systems. These are collection efficiency, sample stability, recovery, minimal interference and an understanding of the mechanism of collection. Ideally, the first three would be 100% and there would be no interference or change in the material when collected. Sample stability becomes increasingly important as the time between sampling and analysis increases. Effects of temperature, trace contaminants and chemical reactions can cause the collected species to be lost from the collection medium or to undergo a transformation that will prevent its recovery. Nearly 100% recovery is also required because a variable recovery rate will prevent quantification of the analysis. Interference should be minimal and, if present, well understood.

3.2 General Sampling Considerations for Particulate Pollutants

When one is sampling for particulate matter in the atmosphere two types of information are of interest - the mass concentration and the chemical composition of the particles. This information is valuable for a variety of problems : effects on human health, identification of particulate matter sources, understanding of atmospheric haze and particle removal processes.

The primary approach is to separate the particles from a known volume of air and subject them to weight determination and chemical analysis.

Airborne particles may be collected by impingers, electrostatic precipitators or filters. Filters are currently much favoured because of their ease of use and high efficiency of collection for small particles. Organic membrane filters are suitable for the collection of airborne particles as small as 0.03μm in diameter, although efficiency is reduced with increasing pore size of the filter and with increasing particle velocity at the face of the filter and thus sampling rate. Glass fibre filters, although not having such a high collection efficiency, allow very fast passage of air and are used with high volume samplers.

An important consideration in selecting a filter medium for trace metal analysis, is the background metal content of the filter material. Cellulose paper filters are recommended because of low levels and homogeneous distribution of the metallic impurities in them.

Sampling of particulate matter from gas streams such as stack gases should be isokinetic, but for sampling relatively stagnant ambient air this is not essential and generally not feasible as wind velocity and direction are seldom constant. Particles may be lost in a sampler by electrostatic attraction to surfaces within the sampler. Ideally, therefore, particles should reach the collector as soon as possible after entering the sampling apparatus. Additionally, all sampling equipment should be rigorously tested for leaks before use if accurate quantitative sampling is required.

For trace metal-in-air sampling, the required equipment is :

- pump
- filter holder
- filter
- flow meter
- gas meter

After sampling, the filter holder would be sealed and the volume of air sampled noted. The filter would then be unloaded in a clean area and transferred to the laboratory for analysis.

3.3 Sample Siting Requirements

Sampling site selection is dependent upon the purpose or use of the results of the monitoring programme. Sampling activities are typically undertaken to determine the ambient air quality for compliance with air quality standards, for evaluation of the impact of a new air pollution source during the preconstruction phase, for hazard evolution associated with accidental spills of chemicals and for research on atmospheric chemical and physical processes. The results of ambient air monitoring can be used to judge the effectiveness of the air quality management approach to air pollution problems. The fundamental reason for controlling air pollution sources is to limit the build-up of contaminants in the atmosphere so that adverse effects are not observed. This suggests that sampling sites should be selected to measure pollutant levels close to or representative of exposed populations of people, plants, trees, materials, structures etc. Sampling sites require electrical power and adequate protection, even a shelter may be necessary. Permanent sites will require adequate heating and air conditioning to provide a stable operating environment for the sampling and monitoring equipment.

3.4 Site Selection for this Study

The aim of this project was, as far as possible, to effectively measure air emissions from the College science laboratories. The science block at the Llandaff site of CIHE houses three teaching laboratories with fume cupboards that ventilate via ducting leading to emission points on the flat roof of the building. Each of the nine fume cupboards ventilate independently culminating in nine separate emission points on the flat roof. Also situated on the roof is a tank room, where it was decided to house all the sampling equipment with the exception of the collection media. This tank proved ideal in that it provided power supplies for the pumps and afforded complete weather protection for the majority of the equipment. Exit holes were drilled in the wall of the tank room to allow long lengths of PVC tubing to be fed out to the remote sampling stations housing the loaded filter holders. The tubing was connected to plastic barbed connectors screwed into the filter holders and the other end connected to a gas meter with a specially made fitting to provide an air-tight seal. Each sampling station was completely portable and could easily be moved to its desired position prior to a sampling run.

A roof plan is included (Figure 3.1) indicating the positions of the individual fume cupboard emission points in relation to the central tank room. A position at the rear of the tank room was designated as a control sampling position in order to measure background levels of three element pollutants.

Table 3.1 below relates the nine fume cupboard emission points to their respective laboratories.

Table 3.1 **LISTING OF FUME CUPBOARD EMISSION POINTS WITH THEIR LABORATORIES IN SCIENCE BLOCK**

Emission Point	Laboratory
FC 1	) Chemical research laboratory
FC 2	) T0.05 (Ground Floor)
FC 3	)
FC 4	) Clinical Chemistry laboratory
FC 5	) T2.31 (Second Floor)
FC 6	)
FC 7	)
FC 8	) Biochemistry laboratory
FC 9	) T2.26 (Second Floor)

FC - Fume cupboard

3.5 Sampling Apparatus

The maximum number of sample collections carried out at the same time were three. These consisted of two sampling stations placed alongside individual emission points and the control sampling station positioned behind the tank room. The complete list of apparatus used is as follows :

- 2 x MCS 10 Programmable pumps 0-15 litres/min
- 1 x High volume pump 0-50 litres/min
- 6 x Plastic filter holders 47mm diameter
- Cellulose ester filters 0.8μm 47mm diameter

  Purchased from : SKC Limited
  Blandford Forum
  Dorset

- 3 x G4 type gas meters (m^3)

  Purchased from : UGI Meters Limited
  London

- Inlet/Outlet gas fittings for above
- Flow meter (litres/min)
- 3 x 30m 6mm internal diameter PVC tubing
- Metal stands, bosses and clamps
- Weather shields for filter holders

3.6 Sampling Methodology

All the pumps and gas meters were set up on a table in the tank room where they were accessible to power supplies (Figure 3.2). The gas meters were fitted with customised gas fittings that included reducing adapters to accommodate connection to the 6mm internal diameter PVC tubing. Small

lengths of PVC tubing connected each pump to the outlet of a gas meter. Each pump was calibrated appromimately to 15 litres/min with the aid of a flow meter prior to connection to the gas meter.

A 30m length of PVC tubing was then connected to the inlet of each gas meter and fed through exit holes in the tank room wall situated just above the sampling apparatus. The length of tubing connected to the high volume pump (0-50 litres/min) system was routed to the rear of the tank room for connection to the filter holder situated at the control position indicated on the roof plan (Figure 3.1 and Figure 3.3). The remaining two lengths of tubing were routed across the flat roof to the filter holders positioned alongside one of the emission duetings (Figure 3.5). These two sampling systems were systematically rotated around each of the emission ductings for separate sampling runs. Each length of tubing was secured to the flat roof using weighted fixtures. Each system was then tested by drawing in white smoke from capsules purchased for this purpose and checking each connection for signs of leakage.

The only sampling position to remain constant was the control sampling station at the rear of the tank room. Each filter holder was carefully loaded with a filter paper using plastic tipped forceps in the laboratory before being transported to its sampling position for connection to the sampling system. The filter holders were then screwed to plastic connectors inserted into the PVC tubing, protected by weather shields and set up at a sampling position using metal stands, bosses and clamps (Figure 3.7). Once the connections were all effected, the pumps were either set automatically to run for a 24 hour period, or manually if longer sampling times were required.

Initial meter readings were recorded from each of the gas meters used in the sampling run, then all pumps were started simultaneously and left running for

the duration of the sampling run. At the end of the designated sampling period, the pumps either automatically cut out or were manually switched off. The new meter readings from each gas meter were then recorded. Each filter holder was then carefully unscrewed from its connector and transported back to the laboratory before removing the filter paper for subsequent chemical analysis.

Freshly loaded filter holders were prepared to replace those taken for analysis and new sampling runs started as described previously.

3.7 Controlled Experiments to Measure Efficiency of Fume Cupboard Ventilation

During the course of this study, a major question arose as to whether measurements taken at the emission points on the roof were actually representing levels of metal pollutant that could be generated within the laboratories. The only way to resolve this question was to sample air within the laboratory and at its emission point and compare their analysed results.

To do this successfully, a means of generating a high level of "metal pollutant" needed to be devised. It was decided to incorporate the use of the atomic absorption spectrometer sited in fume cupboard FC 6 to atomise metals from solutions made up in high concentration. These metal solutions were made up from compounds of lead and chromium to a concentration of 1000$\mu g\ cm^{-3}$.

The procedure undertaken was to draw the concentrated metal solutions through the flame of the spectrophotometer to atomise the metal ions and to "flood" the air in the fume cupboard with a high metal content. While this

atomisation of solution was being carried out, the air in the fume cupboard was ventilated to the roof via the emission ducting.

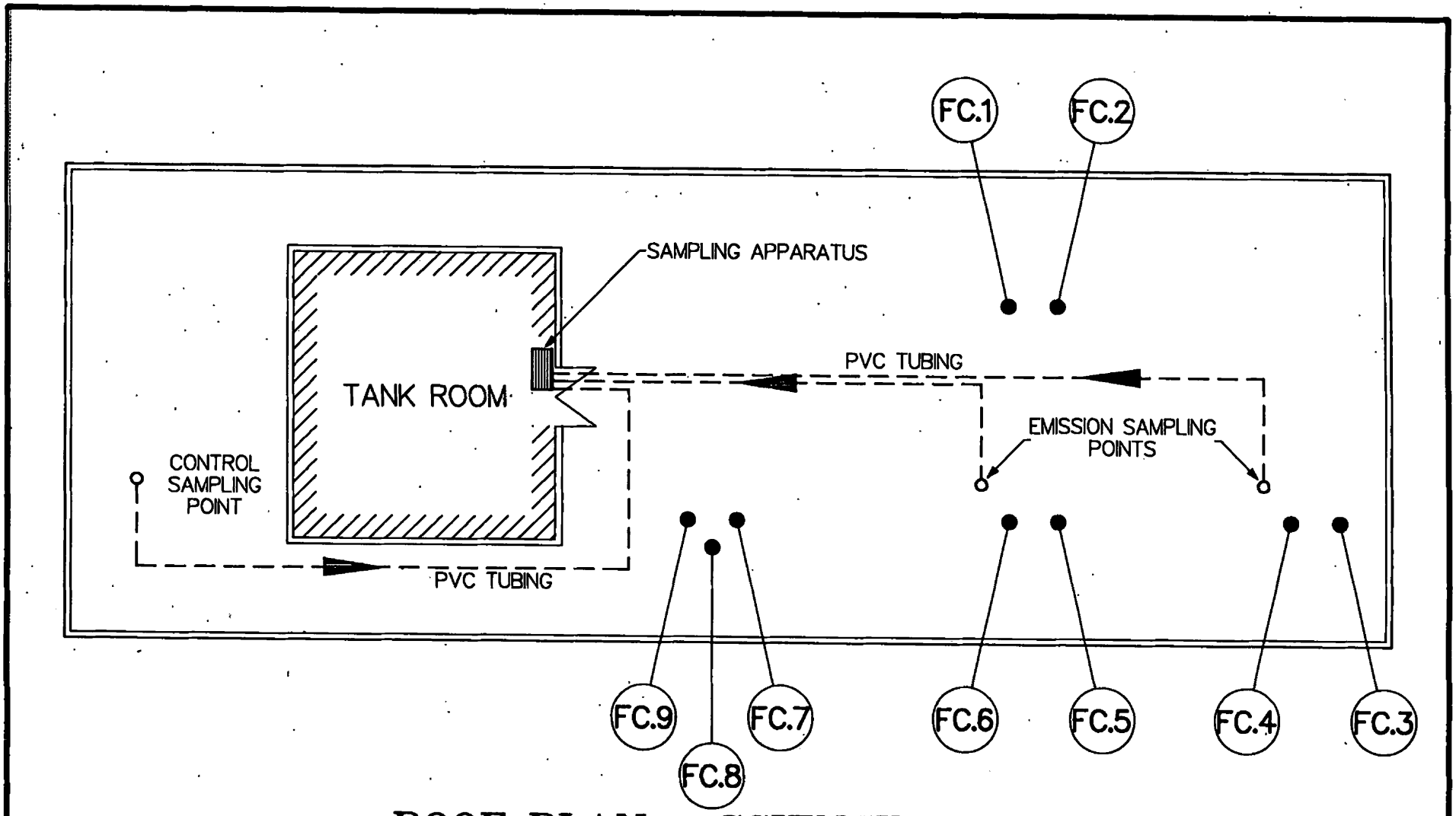
Two sampling stations were positioned either side of the emission ducting and sampling runs carried out for a period of four hours in the same manner as described previously. At the end of this period, the total volume of air sampled was noted and the filters analysed for whatever metal contained in the solution being atomised at that time. The experiment was carried out for both lead and chromium solutions.

Another set of experiments were carried out with sampling apparatus set up within the fume cupboard. A collection hood was constructed directly above the flame of the spectrophotometer in order to sample the majority of the metal ions being given off. A schematic layout of this apparatus is shown in Figure 3.8, while further photographic detail is shown in Figures 3.9 and 3.10.

The two sampling stations were again set up at the emission point on the roof, hopefully to collect any metal ions not picked up by the internal sampling apparatus.

All three sampling pumps were started simultaneously while the metal solution was being atomised by the flame of the spectrophotometer. Again four hour sampling runs were carried out for both the lead and chromium solutions. All filters were then analysed for the metal in the solution being aspirated.

Comparison of all the results obtained from the above experiments should provide an understanding of movement of metal polluted air from the laboratory to its emission point.



ROOF PLAN – SCIENCE BLOCK
C.I.H.E – LLANDAFF

FIGURE 3.1

Figure 3.2 Gas meters and pumps set up inside tank room adjacent to power supply. Exit holes directly above.

Figure 3.3 Control sampling position at rear of tank room.

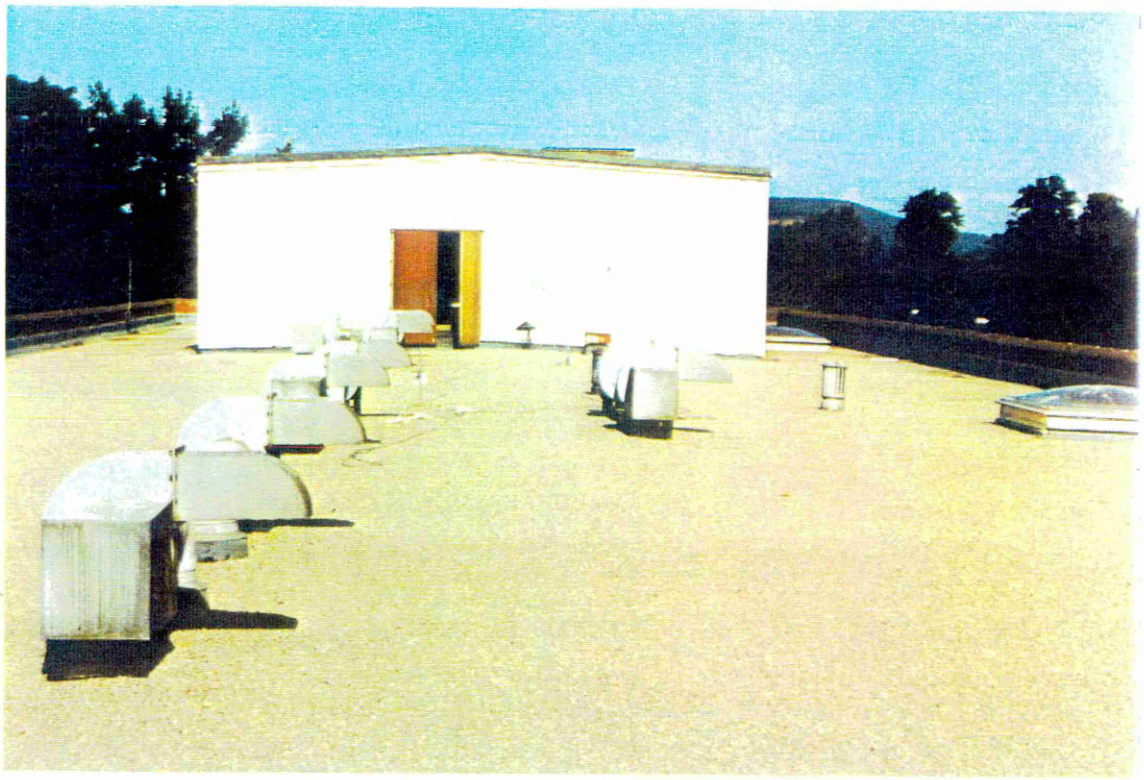


Figure 3.4 Emission ductings from nine fume cupboards situated in Science laboratories.

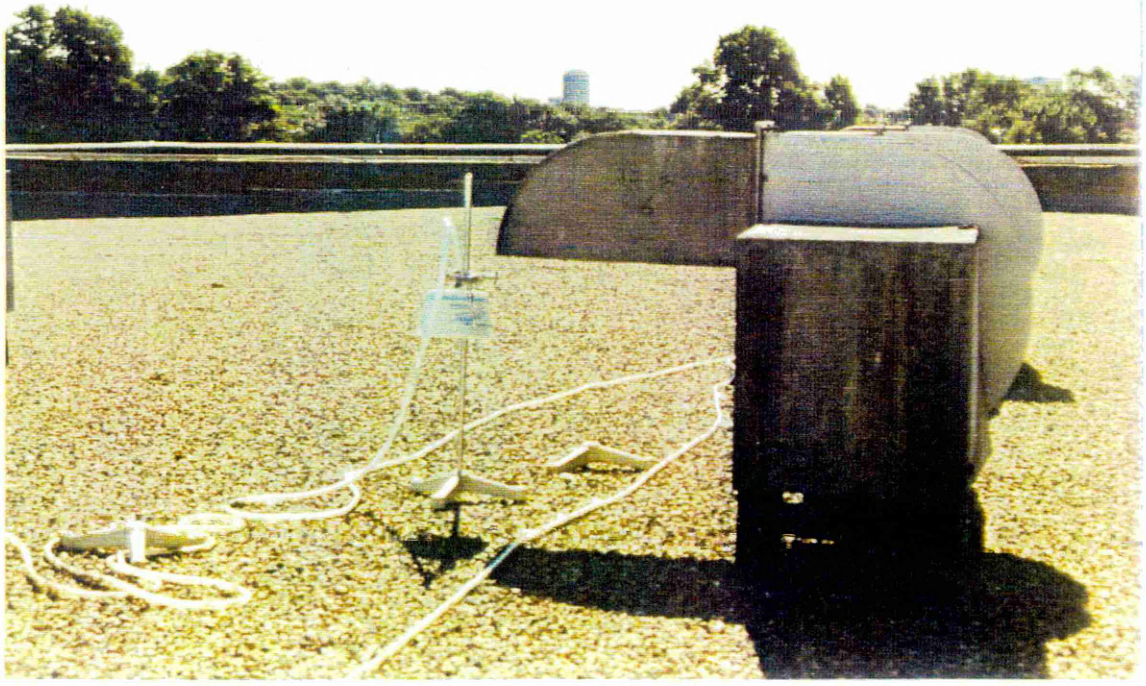


Figure 3.5 Sampling station set up adjacent to emission ducting.

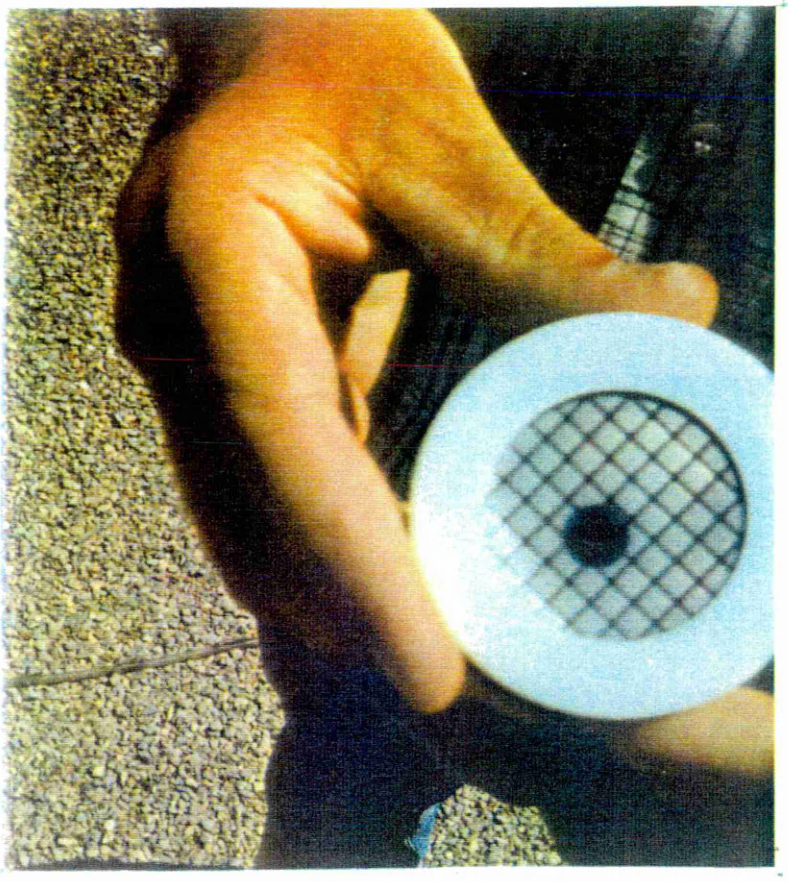
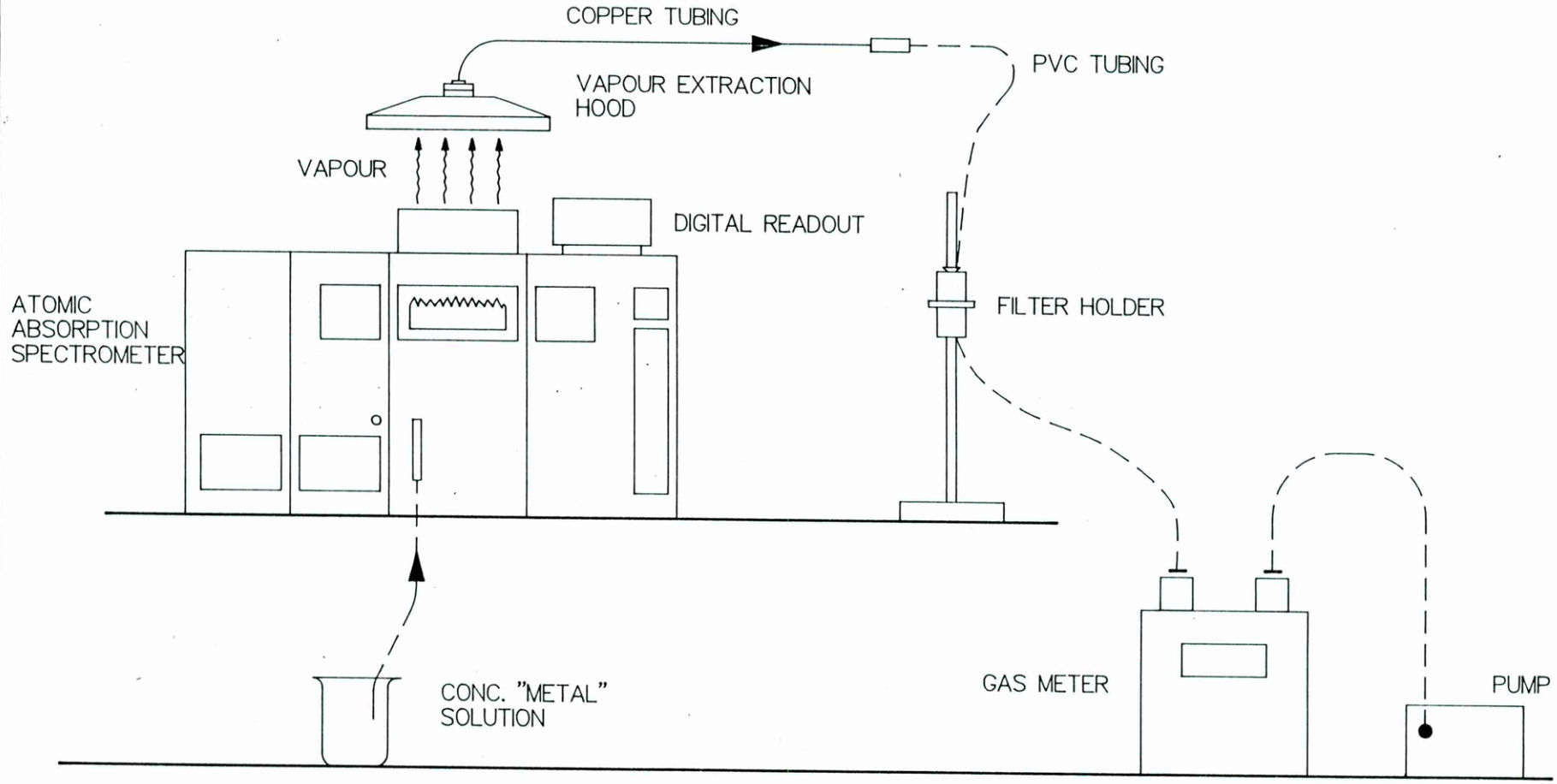


Figure 3.6

Unloaded filter holder with screw-in plastic connector

Figure 3.7

Changing filter holder between sampling runs



APPARATUS LAYOUT FOR CONTROL EQUIPMENT

FIGURE 3.8

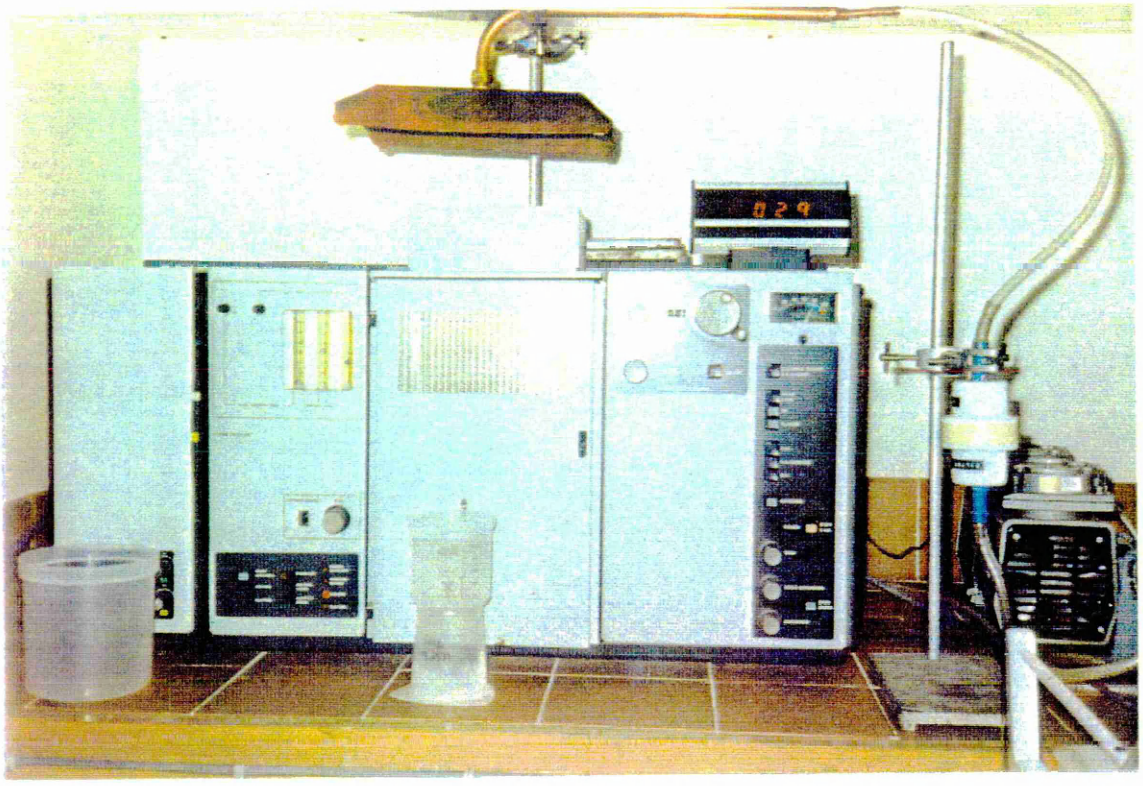


Figure 3.9 Collection hood situated directly above spectrophotometer flame while aspiration of metal solutions takes place.

Figure 3.10 Full sampling assembly for internal sampling of "metal-enriched" air.

CHAPTER FOUR

METHODOLOGY FOR ANALYSIS OF COLLECTED SAMPLES

4.1 Introduction

In recent years increasing emphasis has been placed on the characterisation of trace metals in the atmosphere. Atomic Absorption Spectroscopy (AAS), because of its sensitivity, general lack of interferences, low cost and simplicity of operation, is an excellent technique for the measurement of a large number of elements. The analysis of a variety of metals in atmospheric particulate matter is an area in which AAS is a particularly useful technique. Several investigators (eg. Beyer, 1969 *[24]*; Burnham et al, 1970 *[25]*; Carlson and Black, 1970 *[26]*) have used AAS to measure a number of metals in atmospheric particulate matter collected from different locations. Hwang (1972) *[27]* has extensively reviewed the use of various AAS procedures to measure trace metals in atmospheric particulate matter.

4.2 Atomic Absorption Spectroscopy

In its common form, atomic absorption spectroscopy functions as follows. Air is blown through a venturi and the sample solution (analyte) is drawn into the throat of the venturi and into the air stream as a spray of fine droplets. A large fraction (~ 90%) of the drops fall out of the air stream in the cloud chamber, but the very small ones remain suspended. The air is mixed with a fuel gas and the mixture passes through a narrow slot where it is ignited to form a flame. In the flame the sample vaporises and forms a cloud of atoms in the gaseous state. Through the flame is passed a light beam that contains light of the wavelength corresponding to the energy required to raise the atoms of the particular element being analysed from their ground state to an excited state. This

wavelength is observed by the monochromator and the amount of energy absorbed by the flame is determined, hence the number of atoms in the ground state in the flame. A hollow cathode lamp may be used to obtain the light of the required wavelength. This is a lamp with a cathode that consists of a hollow chamber containing the element being determined, so that the emission radiation of the element is obtained. The oxidant-fuel mixtures most commonly used are air/acetylene and nitrous oxide/acetylene. A photocell, amplifier and readout device measures the intensity of the absorbance produced. A signal obtained in the same manner, but with pure solvent only (no absorption) permits the calculation of percent absorption, which is an indication of analyte concentration in the solution. The arrangement of the various parts of the instrument is shown below :

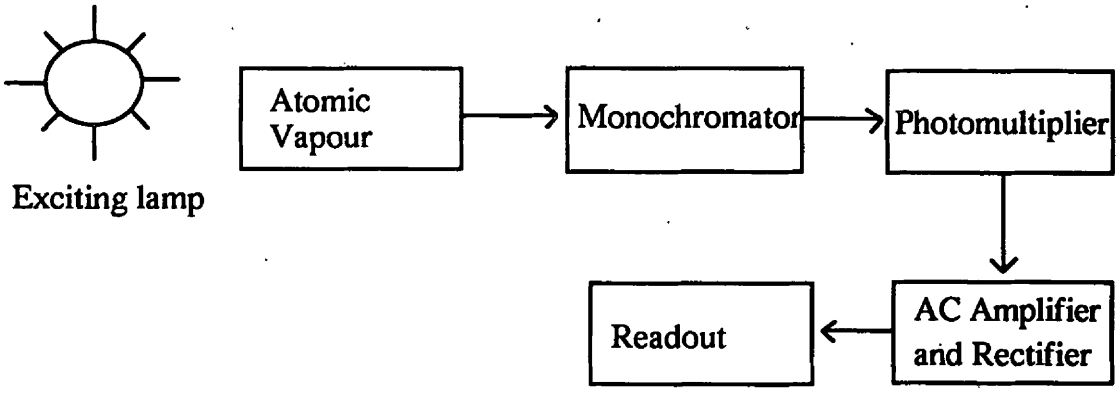


Figure 4.1 An atomic absorption spectrometer block diagram of the light path, from the exciting lamp to the final readout

There are a number of potential interferences in this technique; they may be classified in three categories :

ionisation;
chemical;
matrix.

In ionisation interference the element absorbs energy from the flame and becomes ionised. The ions of the element absorb energy at a different wavelength from that of the ground state so that the monochromator and photomultiplier do not "see" this absorption of energy. In addition the ion, in falling back to the ground state, may emit energy of the same wavelength as the analytical line whose absorption is being measured. Ionisation occurs most easily in the alkali or alkaline earth elements. Lowering the temperature of the flame will reduce ionisation, but will increase the probability of chemical interferences. Chemical interferences arise when the fraction of the element that forms atoms in the ground state in the flame is different with the sample than with the standard solutions. This may result in a depression or an enhancement of the signal. This type of interference may be overcome by chemical treatment or higher flame temperatures.

Matrix effects are due to chemical and physical differences between the sample and the standard. For example, if the sample has a high solids content then there may be scatter in the flame from the large number of solid particles formed. This interference is best overcome by the use of a background corrector. In this technique the apparent absorption of a wavelength close to the analytical wavelength is measured. This gives a measure of the non-specific absorption in the flame and can be used to correct the apparent absorption at the analytical wavelength. Many instruments are equipped to carry out this background correction on an automatic basis.

Recommended wavelengths and detection limits for some elements analysed by AAS are listed in Table 4.1.

TABLE 4.1 DETECTION LIMITS AND RECOMMENDED WAVELENGTHS FOR SOME ELEMENTS USING DIRECT ASPIRATION AND A FLAME

ELEMENT	WAVELENGTH/nm	FLAME	DETECTION LIMIT $\mu g\ m^{-3}$
Ag	328.1	1	2
Al	309.3	2	20
As	193.7	4	50
B	249.7	2	1500
Ca	422.7	1	0.5
Cd	228.8	1	2
Co	240.7	2	10
Cr	357.9	1	3
Cu	324.7	1	1
Fe	248.3	1	5
Hg	253.6	3	250
Mg	285.2	1	0.1
Mn	279.5	1	2
Mo	313.3	2	20
Na	589.0	1	0.2
Ni	232.0	1	2
Pb	283.3	1	10
Sb	217.6	1	40
Se	196.0	4	50
Sn	224.6	3	10
V	318.4	2	40
Zn	213.9	1	1

4.3 Advantages of the AAS Method

The AAS method of elemental analysis now pervades every field of chemistry, geology, biology and medicine. Compared to competing methods, AAS has high sensitivity and high precision, and it can be applied to some 70 elements. The operating procedure is simple and fast, but sample preparation in most cases requires some chemical manipulation. Interferences are at a minimum, and the sample weight required is small.

In specific terms, sensitivity for the various elements ranges from about $20\mu g\ m^{-3}$ down to about $0.005\mu g\ m^{-3}$ and no more than about $1cm^3$ of test solution is needed for a determination. A precision of 1% relative standard deviation (RSD) can be obtained with the flame technique.

The operating procedure, once the sample is in solution and made up to standard volume, is simple and rapid. Throughput of samples by the flame technique is about four per minute. Furthermore, an inexperienced operator can be trained quickly; the more difficult job of sample preparation and organisation of the work may require the services of a professional chemist.

Cost of equipment can be relatively low, and a basic low-cost instrument is capable of performance near the equal of the most elaborate, although without certain automatic features that add a good deal of convenience. These additions include PC computers, automatic control of furnace temperatures and automatic sample changers. If the laboratory interest is in many elements, the necessary library of hollow-cathode lamps can amount to a significant sum.

AAS is primarily a method for solutions which are homogeneous, or can be made so. Compared to solutions, inhomogeneity due to segregation presents severe problems for all solid samples.

In any method involving comparison of an unknown to synthetic standards, a basic requirement is that gross composition of the latter must match the unknown in order to avoid interferences. With solutions, the unknown and standards can be matched easily by a process called standard additions, in which the sample carrying the unknown is doped with known additions of the analyte and the unknown's concentration established by extrapolation of the resulting curve. This process is impractical with solid samples.

4.4 Limitations of the AAS Method

Changing the equipment set-up from one element to another requires changing the exciting lamp, adjusting the wavelength setting, maximising of the signal and making one or more calibrations. None of these require much time or effort, although lamp warm-up for a single-beam illuminating system may take half an hour. However, some single-beam instruments can be equipped with a turret arrangement carrying several lamps in a warm-up condition.

Where the AAS method falls down completely is that it is solely used for quantitative analysis. Other methods of analysis need to be used to qualify what elements are present.

4.5 Reagents

Concentrated Nitric acid "Spectrosol" grade (S.G. 1.42).

30% w/v Hydrogen Peroxide "Spectrosol" grade (100 vols).

Atomic Absorption Spectrometry Standard solution (1000 $\mu g\ m^{-3}$) for the following metals :

Al, Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn.

All above purchased from BDH Chemicals.

4.6 Prepared Solutions

5% v/v Nitric Acid

$50cm^3$ of concentrated nitric acid (S.G. 1.42) was diluted to 1 litre with distilled water and mixed thoroughly.

50% v/v Nitric Acid - hydrogen peroxide solution

$50cm^3$ of concentrated nitric acid (S.G. 1.42) + $2cm^3$ of 30% v/v Hydrogen Peroxide solution were made up to $100cm^3$ with distilled water.

"Working" Standard metal solutions ($50\mu g\ m^{-3}$)

For all elements excepting cadmium, $50cm^3$ of the Atomic Absorption Standard solution ($1000\mu g\ m^{-3}$) was added to a 1 litre volumetric flask and made up to volume with 5% v/v nitric acid.

"Working" Standard Cadmium solution ($20\mu g\ m^{-3}$)

$20cm^3$ of the Atomic Absorption Standard cadmium solution was added to a 1 litre volumetric flask and made up to volume with 5% v/v nitric acid.

Calibration solutions from "working" standard metal solutions

2, 5, 8 and $10cm^3$ of each "working" standard were pipetted into separate $100cm^3$ volumetric flasks. These were made up to volume with 5% v/v nitric acid and mixed thoroughly.

These corresponded to concentrations of $1\mu g\ m^{-3}$ (1 ppm), $2.2\ \mu g\ m^{-3}$ (2.5 ppm), $4\mu g\ m^{-3}$ (4 ppm) and $5\mu g\ m^{-3}$ (5 ppm) for all elements except cadmium.

The concentrations for cadmium were $0.4\mu g\ m^{-3}$ (0.4 ppm), $1\mu g\ m^{-3}$ (1 ppm), $1.6\mu g\ m^{-3}$ (1.6 ppm) and $2\mu g\ m^{-3}$ (2 ppm). The calibration solutions were always freshly prepared before each analytical run.

4.7 Sample Preparation

Filter samples were obtained by the methodology described in Chapter Three. To minimise contamination the filter samples were not unloaded from the sampling heads until they had been transported to the laboratory. Each filter head assembly was carefully opened and the filter paper removed with plastic-tipped forceps. Each filter paper was placed in a $150cm^3$ squat-form beaker and $5cm^3$ of the 50% v/v $HN0_3/H_2O_2$ solution added. The beaker was covered with a watch glass and placed on a hot plate and the filter and solution allowed to simmer gently until the filter had completely dissolved (about 20 minutes). The resultant solution was heated further until brown nitrogen dioxide fumes ceased to be evolved. The watch glass was then removed from

the beaker and the solution allowed to simmer further until its volume had been reduced to approximately 1.0cm^3.

The beaker was removed from the hot plate and allowed to cool. The contents of the beaker were then washed into a 10cm^3 volumetric flask using distilled water. This 10cm^3 flask was then made up to volume with distilled water, making the final concentration of the solution approximately 5% v/v $HN0_3$. This was to equate with the calibration standards which were also made up in 5% v/v $HN0_3$.

The solution was then transferred to a 30cm^3 plastic universal bottle for storage until analysis was carried out. Each bottle was carefully labelled with sampling location and date and allocated a number. Large numbers of samples were collected and prepared before analysis was carried out.

Several blank samples were prepared by placing unused filters in 5cm^3 of 50% v/v $HN0_3/H_2O_2$ solution and digested and made up to solution as described above.

4.8 Analysis of Samples using Atomic Absorption Spectrometry

The spectrophotometer used for this analysis was a Pye Unicam Model SP9 linked to a BBC computer. Four hollow-cathode lamps of the elements required to be measured were fitted to the turret assembly of the spectrophotometer. Power was turned on at least one hour before usage to allow the lamps to warm up.

The acetylene and air supplies were turned on and their flow rates adjusted to the levels recommended by the operator's handbook. The flame was ignited and allowed to settle for at least 15 minutes before use.

The wavelength and lamp current were set by information provided by the computer software with respect to the elements being measured. The turret was revolved until the correct hollow-cathode lamp was lined up with the flame.

Sampling commenced by introduction of a solvent blast (in this case 5% v/v $HN0_3$) to the flame via an aspiration tube placed in the solvent which drew it up into the flame where the solution was atomised. An absorbance reading was displayed on the digital panel of the instrument and a hard copy simultaneously printed out via the computer. The four calibration solutions are then passed through the flame in the same manner and the absorption information obtained is used by the computer to produce a calibration graph. The sample solutions are then passed through the flame sequentially where the absorbances are compared with those of the calibration solutions and their concentrations calculated from the graph.

Finally the blank filter solutions were sampled and their averaged absorbance deducted from that of the sample solution for the final calculation.

4.9 Calculation of sample concentration in Air

To calculate the concentration of the element in the volume of air sampled, the following equation is used :

$$\text{Concentration of element in air (ng m}^{-3}\text{)} = (Cs - Cb) \times \frac{Vs}{Va} \times 10^3$$

where

Concentration of element in the sample solution ($\mu g\ m^{-3}$) = Cs

Concentration of element in blank filter sample ($\mu g\ m^{-3}$) = Cb

Volume of sample solution (cm^3) = Vs

Volume of air sample (litres) = Va

CHAPTER FIVE

RESULTS

5.1A Collection of emission air samples during April 1994

During this survey two sample collections were carried out over 24 hour periods. This consisted of one collection carried out at the control point of the tank room while the other collection was carried out at one of the fume cupboard emission points. These points were changed daily the control point remaining fixed. Both MCS 10 programmable pumps used in this survey were set at approximately 13-14 litres/min and each run limited to 24 hours, so that the maximum amount of air passing through the filters was 20,000 litres. Full details of each sampling run during this period is exhibited in Table 5.1A.

5.1B The filters were removed from their holders at the end of each sampling run and analysed by the method detailed in Chapter 4. By using the calculation set out in 4.9, the weight of metal pollutant per cubic metre of air sampled was estimated. These results are expressed as ng m^{-3} and appear in Table 5.1B.

5.2A Collection of emission air samples during May-June 1994

In this survey three sampling runs were carried out simultaneously by means of the introduction of a high volume pump used solely for the air collection at the control point. This allowed two fume cupboard emission points to be sampled at the same time. The high volume pump was set at 20-25 litres/min allowing a greater amount of air passed at the control point compared with the two smaller pumps used in the FC emission systems.

The pumps were all run in a manual mode for this survey, allowing for variation in sampling time as desired. Sampling runs were extended in some cases up to

two weeks to increase particulate collection and hopefully to improve accuracy of the reported results.

Full details of this survey are listed in Table 5.2A.

5.2B Analyses of the filters were carried out as described previously and the results reported in Table 5.2B.

5.3A **Controlled experiments sampling air contaminated with atomised chromium or lead metal ions**

These experiments were carried out to measure efficiencies of fume cupboard ventilation which allowed collection of excessive amounts of metal, thereby resulting in higher absorption measurements. These higher concentrations fell well within the measurement capabilities of the analytical equipment allowing assessment of the acid digestion procedure.

Full details of the controlled experiments are listed in Table 5.3A.

The calculated results from the above experiments are shown in Table 5.3B.

Atomic absorption results for each element are listed in Tables 5.5 to 5.11.

TABLE 5.1A EMISSION AIR SAMPLING DATA

Sample No.	Date	Sampling Position	Litres of Air Passed
001	28.03.94	Control Behind tank room	19,187
002	28.03.94	FC3 T2.31	17,091
004	29.03.94	FC4 T2.31	16,948
005	29.03.94	Control	20,196
006	30.03.94	Control	19.889
007	30.03.94	FC5 T2.31	17,385
008	6.04.94	Control	19.969
009	7.04.94	FC6 T2.31	17,473
010	7.04.94	Control	20.274
011	11.04.94	FC1 T0.05	16,499
012	11.04.94	Control	16,923
014	12.04.94	FC2 T0.05	18,802
015	12.04.94	Control	19,195
016	13.04.94	FC7 T2.26	17,837
017	13.04.94	Control	17,916
018	18.04.94	FC8 T2.26	14,779
019	18.04.94	Control	17,118
020	19.04.94	FC9 T2.26	16,982
021	19.04.94	Control	19,219
022	20.04.94	FC3 T2.31	16,874
023	20.04.94	Control	19,223
024	21.04.94	FC4 T2.31	17,605
025	21.04.94	Control	19,349
026	25.04.94	FC9 T2.26	5,909
027	25.04.94	Control	19,377
028	26.04.94	FC7 T2.26	19,390
029	26.04.94	Control	20.110
030	27.04.94	FC8 T2.26	18,919
031	27.04.94	Control	20,091
032	28.04.94	FC1 T0.05	18,704
033	28.04.94	Control	20,144

TABLE 5.1B TRACE ELEMENT ANALYSIS (ng m^{-3})

Sample No.	Al	Cd	Cr	Co	Cu	Fe	Ni	Pb	Zn
001	A		N/D		-	-	A	N/D	-
002	b		N/D		-	-	b	23	-
	s						s		
004	o		-		-	118	o	35	-
005	r		N/D		-	139	r	50	-
006	b		10		-	297	b	20	-
007	a		-		-	63	a	40	-
008	n		N/D		-	120	n	55	-
009	c		23		-	120	c	17	120
010	e		25		-	54	e	39	-
011	s	N	42	N	-	206	s	48	97
012		o	12	o	-	254		47	-
013	T	n	-	n	-	-	T	-	-
014	o	e	64	e	-	27	o	N/D	48
015	o		63		-	146	o	.5	47
016		D	N/D	D	34	62		11	56
017	L	e	N/D	e	50	28	L	6	45
018	o	t	N/D	t	7	223	o	N/D	88
019	w	e	N/D	e	76	602	w	12	93
020		c	N/D	c	6	77		N/D	35
021	F	t	-	t	-	78	F	N/D	-
022	o	e	N/D	e	-	107	o	N/D	-
023	r	d	-	d	-	104	r	N/D	-
024			N/D		-	108		N/D	40
025	A		N/D		N/D	62	A	N/D	36
026	c		N/D		-	-	c	-	-
027	c		N/D		21	114	c	N/D	46
028	u		N/D		21	N/D	u	N/D	10
029	r		N/D		5	N/D	r	N/D	15
030	a		N/D		N/D	N/D	a	N/D	11
031	c		N/D		N/D	N/D	c	N/D	5
032	y		N/D		5	16	y	21	37
033			N/D		5	581		40	20

N/D - None detected

TABLE 5.2A EMISSION AIR SAMPLING DATA

Sample No.	Date	Sampling Position	Litres of Air Passed
034	9.05.94	FC3 T2.31	18,569
035	9.05.94	FC4 T2.31	20,564
036	9.05.94	Control behind tank	32,596
037	10.05.94	FC1 T0.05	19,162
038	10.05.94	FC2 T0.05	20,448
039	10.5.94	Control behind tank	33,100
040	11.05.94	FC3 T2.31	18,742
041	11.05.94	FC4 T2.31	20,430
042	11.05.94	Control behind tank	34,661
043	12.05.94	FC1 T0.05	73,092
044	12.05.94	FC2 T0.05	80,003
045	12.05.94	Control behind tank	128,738
046	16.05.94	FC7 T2.26	18,248
047	16.05.94	FC8 T2.26	20,268
048	17.05.94	FC3 T2.31	18,477
049	17.05.94	FC4 T2.31	20,318
050	17.05.94	Control behind tank	32,934
051	18.05.94	FC1 T0.05	18,576
052	18.05.94	FC2 T0.05	20,421
053	18.05.94	Control behind tank	32,942
054	19.05.94	FC9 T2.26	222,223
055	19.05.94	FC8 T2.26	235,326
056	19.05.94	Control behind tank	391,179
057	31.05.94	FC1 T0.05	18,615
058	31.05.94	FC2 T0.05	20,511
059	31.05.94	Control behind tank	33,012
060	1.06.94	FC6 T2.31	18,568
061	1.06.94	FC7 T2.26	20,235
062	9.06.94	FC3 T2.31	72,186
063	9.06.94	FC4 T2.31	79,893
064	9.06.94	Control behind tank	129,373

TABLE 5.2B TRACE ELEMENT ANALYSIS (ng m^{-3})

Sample No.	Al	Cd	Cr	Co	Cu	Fe	Ni	Pb	Zn
034	A				27	1196	A	8	86
035	b				34	1230	b	N/D	39
036	s				15	1138	s	29	40
037	o				N/D	506	o	8	68
038	r				N/D	592	r	7	73
039	b				N/D	498	b	29	69
040	a				69	1280	a	45	192
041	n				59	1439	n	32	181
042	c				26	1036	c	45	162
043	e	N	N	N	15	386	e	42	60
044		o	o	o	20	395		39	61
045	T	n	n	n	8	332	T	40	55
046	o	e	e	e	55	356	o	N/D	44
047	o				44	405	o	N/D	49
048		D	D	D	N/D	476		N/D	76
049	L	e	e	e	N/D	561	L	27	84
050	o	t	t	t	N/D	462	o	26	70
051	w	e	e	e	N/D	646	w	13	161
052		c	c	c	78	607		22	137
053	F	t	t	t	N/D	610	F	35	140
054	o	e	e	e	6	392	o	42	60
055	r	d	d	d	5	657	r	49	67
056					4	368		44	61
057	A				32	886	A	46	81
058	c				15	873	c	41	73
059	c				12	839	c	56	73
060	u				5	323	u	8	43
061	r				10	410	r	22	44
062	a				11	323	a	24	22
063	c				20	314	c	21	21
064	y				N/D	268	y	20	18

TABLE 5.3A CONTROLLED AIR SAMPLING DATA

Sample No.	Date	Sampling Position	Litres of Air Passed
065*	16.06.94	Internal FC6 Warm air drawn through apparatus	3,056
066*	17.06.94	Internal FC6 Solution of Cr 1000 $\mu g\ cm^3$	3,362
067*	17.06.94	Emission FC6 Solution of Cr 1000 $\mu g\ cm^3$	4,000
068*	17.06.94	Emission FC6 Solution of Cr 1000 $\mu g\ cm^3$	6,150
069*	20.06.94	Internal FC6 Solution of Pb 1000 $\mu g\ cm^3$	1,482
070*	20.06.94	Emission FC6 Solution of Pb 1000 $\mu g\ cm^3$	1,495
071*	20.06.94	Emission FC6 Solution of Pb 1000 $\mu g\ cm^3$	2,372
072*	22.06.94	Emission FC6 Solution of Cr straight through ducting	1,035
073*	22.06.94	Emission FC6 Solution of Cr straight through ducting	1,665
074*	22.06.94	Emission FC6 Solution of Pb straight through ducting	1,050
075*	22.06.94	Emission FC6 Solution of Pb striaght through ducting	1,669

TABLE 5.3B TRACE ELEMENT ANALYSIS (ng m^{-3})

Sample No.	Chromium		Lead
	C_2H_2/Air	C_2H_2/N_2O	C_2H_2/Air
065*	63	98	N/D
066*	83280	63060	-
067*	1000	775	-
068*	244	276	-
069*	-	-	164640
070*	-	-	1538
071*	-	-	2108
072*	2029	2512	-
073*	1502	1562	-
074*	-	-	3905
075*	-	-	839

TABLE 5.4 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF CADMIUM**

Flame : Acetylene/Air
Wavelength : 228.9 nm

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.000		
STD 1	0.177	0.40	0.8
STD 2	0.399	1.00	1.1
STD 3	0.545	1.60	0.3
STD 4	0.635	2.00	0.7
4	0.006	0.01	8.3
5	0.003	0.01	12.9
6	0.001	0.00	20.2
7	0.001	0.00	20.2
8	0.002	0.00	15.7
9	0.000	0.00	0.0
10	0.000	0.00	0.0
11	0.002	0.00	0.0
12	0.001	0.00	0.0
14	0.000	0.00	0.0
15	0.002	0.00	0.0
16	0.003	0.01	12.9
17	0.003	0.01	12.9
18	0.001	0.00	20.2
19	0.001	0.00	0.0
20	0.001	0.00	0.0
21	0.002	0.00	15.7
22	0.003	0.01	12.9
23	0.001	0.00	20.2
24	0.000	0.00	84.9
25	0.001	0.00	47.1
26	0.001	0.00	20.2
27	0.000	0.00	28.3
28	0.001	0.00	60.6
29	0.002	0.00	15.7
30	0.000	0.00	28.3
31	0.003	0.01	12.9
32	0.002	0.00	15.7
33	0.004	0.01	0.0
34	0.001	0.00	0.0
35	0.000	0.00	20.2
36	0.000	0.00	35.4

TABLE 5.4 CONTINUED ...

Sample No.	ABS	CONC (μg cm^{-3})	RSD %
37	0.002	0.00	12.9
38	0.002	0.00	12.9
39	0.001	0.00	47.1
40	0.003	0.01	0.0
41	0.009	0.02	5.2
42	0.002	0.00	23.6
43	0.003	0.01	76.1
44	0.002	0.00	23.6
45	0.005	0.01	0.0
46	0.000	0.00	0.0
47	0.000	0.00	94.3
48	0.000	0.00	35.4
49	0.004	0.01	9.4
50	0.001	0.00	28.3
51	0.002	0.00	64.3
52	0.004	0.01	17.7
53	0.002	0.00	38.6
54	0.006	0.01	0.0
55	0.011	0.02	4.9
56	0.005	0.01	7.4
57	0.000	0.00	0.0
58	0.001	0.00	15.7
59	0.000	0.00	47.1
60	0.003	0.01	10.9
61	0.000	0.00	35.4
62	0.003	0.01	0.0
63	0.002	0.00	0.0
64	0.002	0.00	0.0
Blank Filter 1	0.000	0.00	70.7
Blank Filter 2	0.000	0.00	47.1
Blank Filter 3	0.000	0.00	70.7
Blank Filter 4	0.000	0.00	47.1

GRAPH 5.4 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF CADMIUM

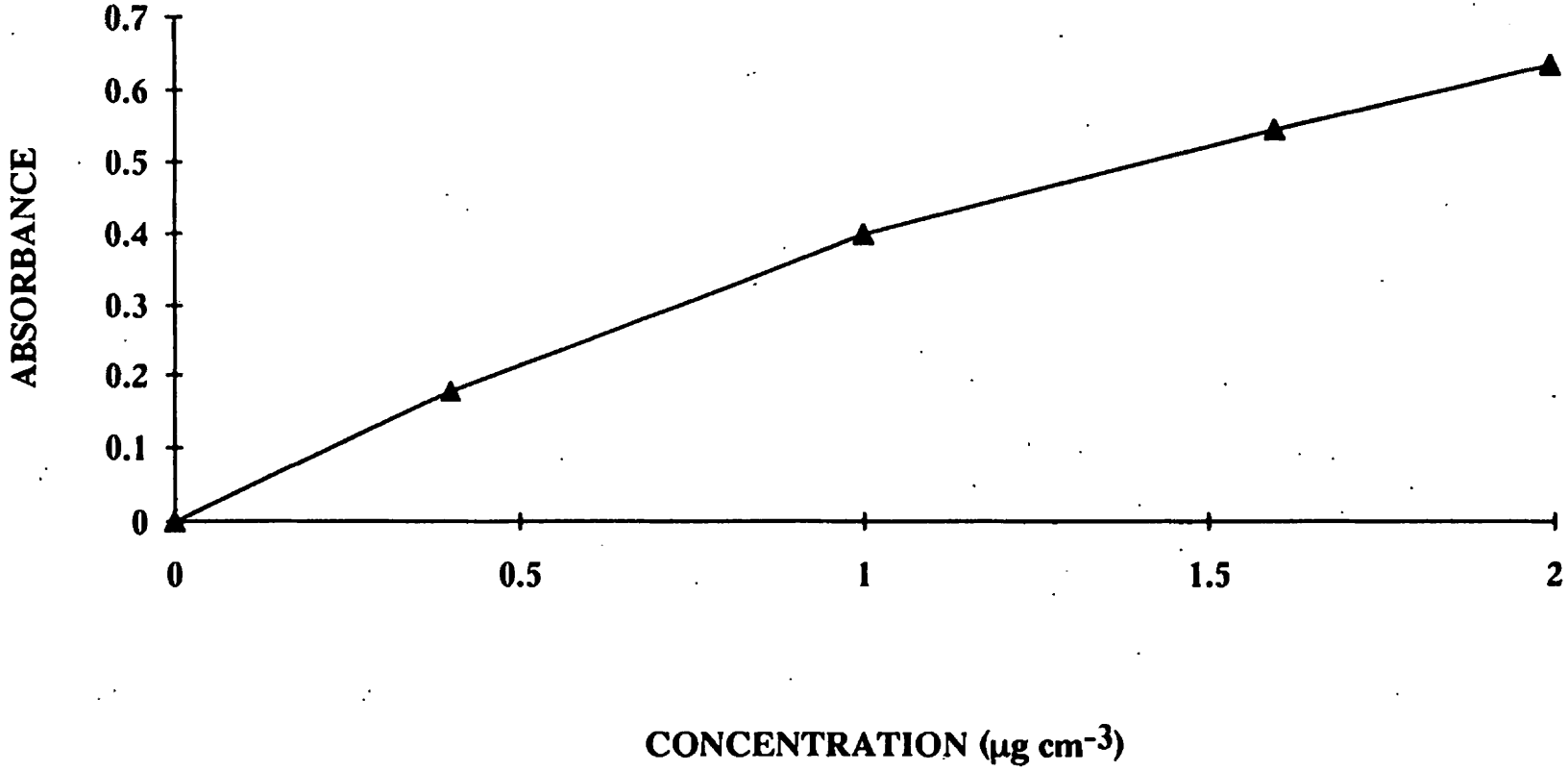


TABLE 5.5 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF CHROMIUM**

Flame : Acetylene/Air
Wavelength : 357.9 nm

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.000		
STD 1	0.051	1.00	0.0
STD 2	0.097	2.50	0.7
STD 3	0.138	4.00	0.5
STD 4	0.167	5.00	0.0
1	0.005	0.08	0.0
2	0.006	0.09	5.7
5	0.002	0.02	25.0
6	0.006	0.10	0.0
8	0.002	0.03	31.4
9	0.008	0.12	4.9
10	0.008	0.13	0.0
11	0.010	0.15	4.3
12	0.010	0.16	0.0
14	0.012	0.20	0.0
15	0.012	0.20	0.0
16	0.002	0.03	0.0
17	0.002	0.03	0.0
18	0.002	0.03	8.3
19	0.002	0.03	0.0
20	0.002	0.03	0.0
22	0.002	0.04	7.4
24	0.002	0.04	7.4
25	0.002	0.04	7.4
26	0.004	0.06	6.7
27	0.004	0.07	0.0
28	0.004	0.06	6.7
29	0.004	0.06	6.7
30	0.004	0.06	6.7
31	0.004	0.07	12.9
32	0.004	0.08	6.1
33	0.004	0.07	0.0
34	0.004	0.08	6.1
35	0.006	0.14	7.4
36	0.005	0.13	0.0
37	0.005	0.13	0.0
38	0.004	0.09	9.4

TABLE 5.5 CONTINUED ...

Sample No.	ABS	CONC (μg cm^{-3})	RSD %
39	0.004	0.08	0.0
40	0.005	0.13	0.0
41	0.006	0.15	0.0
42	0.005	0.13	0.0
43	0.007	0.16	6.7
44	0.005	0.12	8.3
45	0.006	0.14	7.4
46	0.004	0.08	0.0
47	0.006	0.14	7.4
48	0.005	0.13	0.0
49	0.007	0.17	0.0
50	0.007	0.16	6.7
51	0.007	0.17	0.0
52	0.007	0.16	6.7
53	0.007	0.17	0.0
54	0.007	0.17	0.0
55	0.007	0.17	0.0
56	0.007	0.17	0.0
57	0.005	0.12	8.3
58	0.006	0.15	0.0
59	0.005	0.10	0.0
60	0.007	0.16	6.7
61	0.005	0.13	0.0
62	0.008	0.19	6.1
63	0.007	0.16	6.7
64	0.008	0.19	6.1
Blank Filter 1	0.007	0.17	12.9
Blank Filter 2	0.006	0.15	14.1
Blank Filter 3	0.005	0.13	0.0
Blank Filter 4	0.006	0.13	15.7
65	0.007	0.17	0.0
66	0.770	74.18*	0.2
67	0.023	0.55	2.7
68	0.013	0.30	4.3
72	0.016	0.36	0.0
73	0.017	0.40	3.4

GRAPH 5.5 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF CHROMIUM

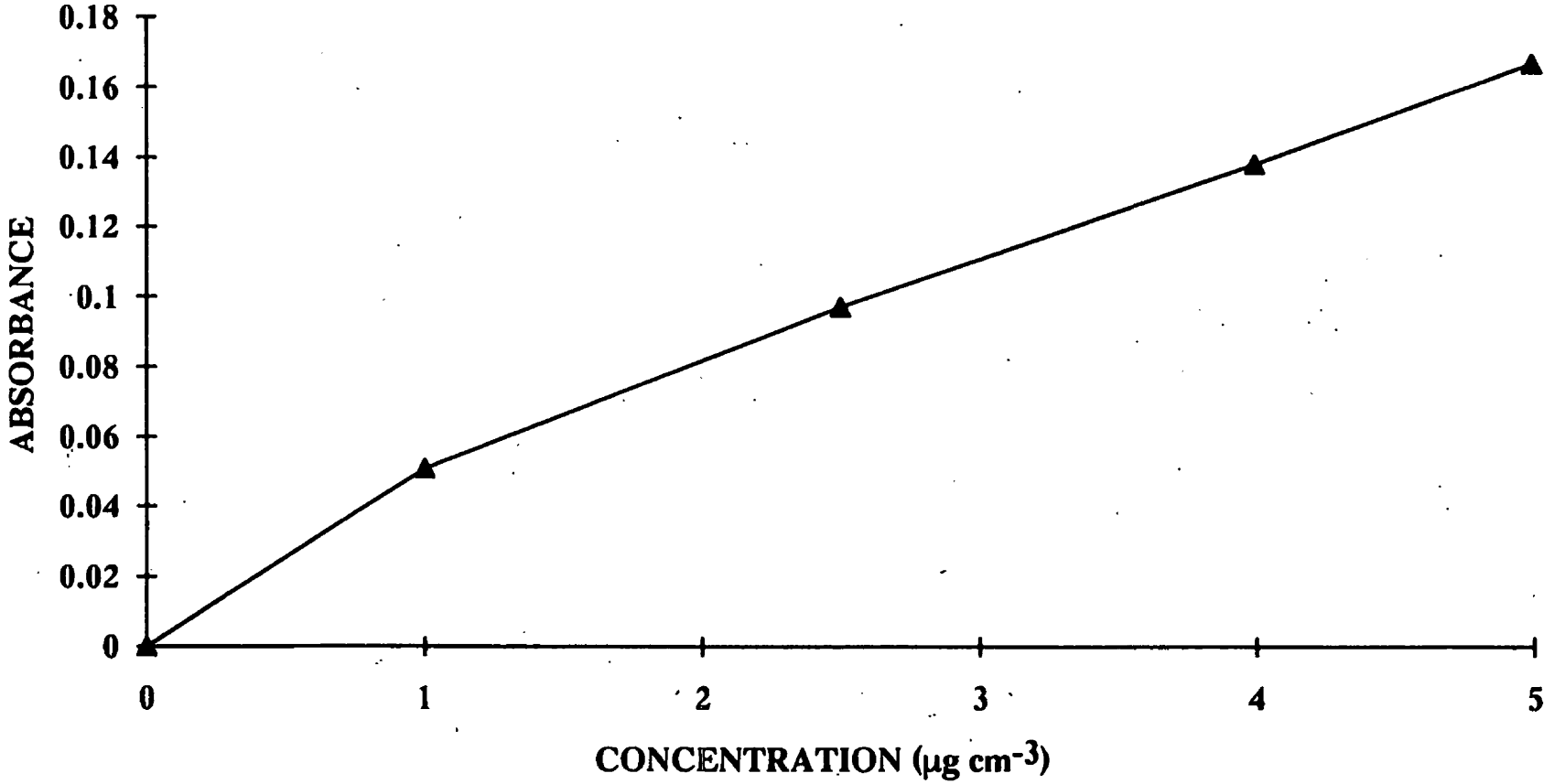


TABLE 5.6 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF COBALT**

Flame : Acetylene/Air
Wavelength : 240.7 nm

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.000		
STD 1	0.070	1.00	0.9
STD 2	0.130	2.50	1.0
STD 3	0.184	4.00	1.1
STD 4	0.214	5.00	0.6
8	0.002	0.02	6.7
9	0.000	0.00	0.0
10	0.001	0.01	0.0
11	0.002	0.02	6.7
12	0.002	0.03	6.1
14	0.001	0.01	0.0
15	0.002	0.03	0.0
16	0.002	0.03	0.0
17	0.002	0.03	0.0
18	0.002	0.02	6.7
19	0.001	0.01	0.0
20	0.001	0.01	0.0
21	0.002	0.02	6.7
22	0.002	0.03	0.0
23	0.002	0.02	6.7
24	0.000	0.01	7.4
25	0.000	0.00	15.7
26	0.000	0.00	9.4
27	0.002	0.02	6.7
28	0.000	0.01	7.4
29	0.002	0.02	6.7
30	0.002	0.02	6.7
31	0.003	0.04	0.0
32	0.002	0.03	12.9
33	0.004	0.05	5.7
34	0.000	0.00	12.9
35	0.000	0.00	28.3
36	0.003	0.03	0.0
37	0.000	0.00	35.4
38	0.00	0.00	15.7
39	0.001	0.01	10.9
40	0.002	0.02	20.2

TABLE 5.6 CONTINUED ...

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
41	0.002	0.02	9.4
42	0.001	0.01	32.6
Blank Filter 1	0.003	0.04	11.8
Blank Filter 2	0.001	0.01	0.0

GRAPH 5.6 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF COBALT

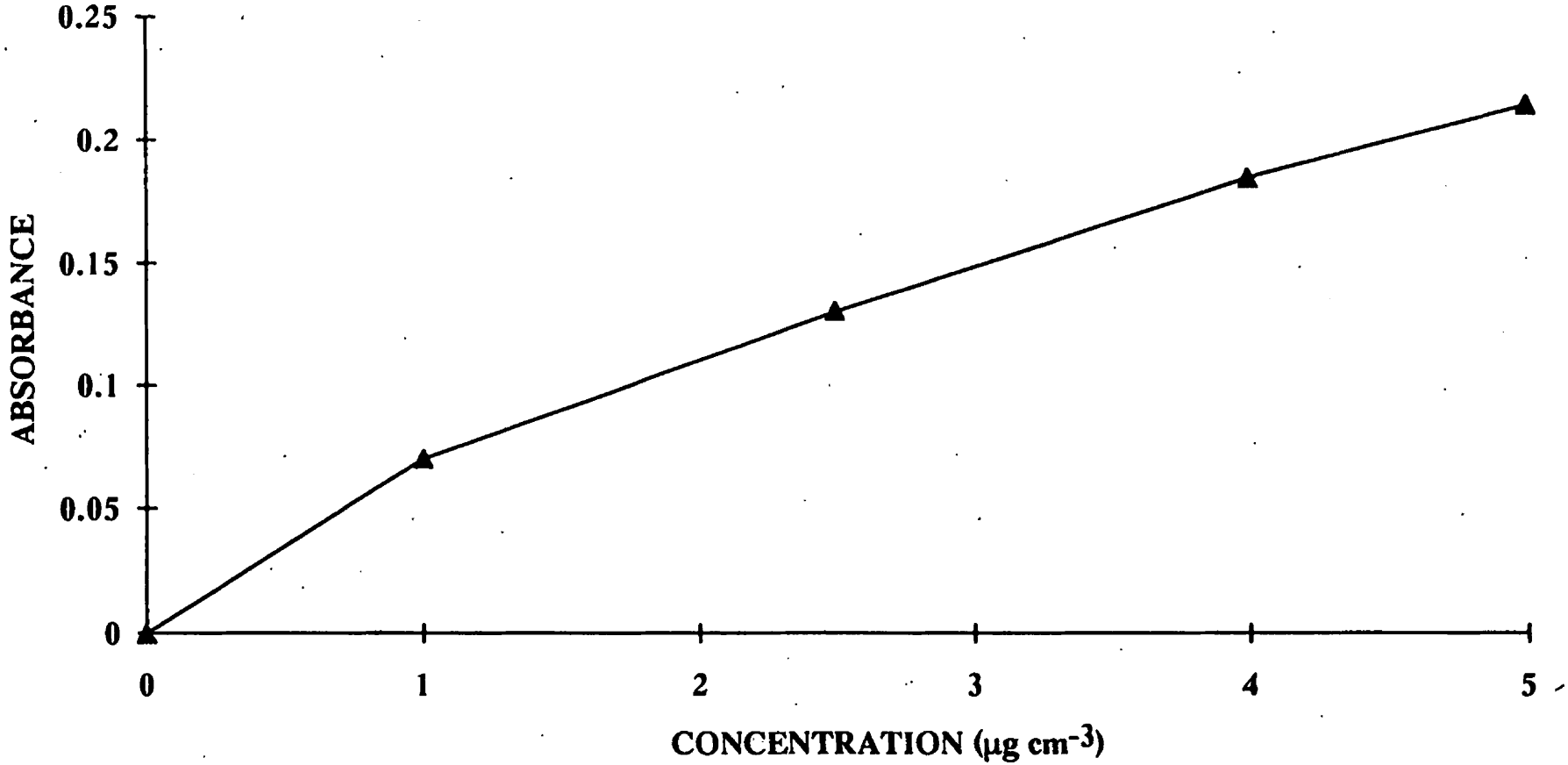


TABLE 5.7 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF COPPER**

Flame : Acetylene/Air
Wavelength : 324.8 nm

Sample No.	ABS	CONC (μg cm^{-3})	RSD %
Blank	0.00		
STD 1	0.065	1.00	0.0
STD 2	0.151	2.50	0.5
STD 3	0.231	4.00	0.3
STD 4	0.286	5.00	0.2
16	0.008	0.12	0.0
17	0.010	0.15	0.0
18	0.005	0.07	0.0
19	0.013	0.19	0.0
20	0.005	0.07	76.0
25	0.004	0.06	0.0
27	0.007	0.10	0.0
28	0.007	0.10	0.0
29	0.005	0.07	0.0
30	0.004	0.06	0.0
31	0.003	0.04	0.0
32	0.005	0.07	0.0
33	0.005	0.07	0.0
34	0.024	0.14	2.6
35	0.028	0.16	0.0
36	0.025	0.14	5.1
37	0.009	0.05	5.7
38	0.010	0.06	0.0
39	0.010	0.06	0.0
40	0.037	0.22	1.7
41	0.035	0.21	1.8
42	0.031	0.18	2.0
43	0.035	0.20	0.0
44	0.043	0.25	3.1
45	0.032	0.19	0.0
46	0.032	0.19	0.0
47	0.031	0.18	2.0
48	0.014	0.08	4.0
49	0.014	0.09	0.0
50	0.012	0.07	4.6
51	0.011	0.06	0.0
52	0.043	0.25	1.5

TABLE 5.7 CONTINUED ...

Sample No.	ABS	CONC (μg cm^{-3})	RSD %
53	0.014	0.08	0.0
54	0.037	0.22	0.0
55	0.035	0.21	1.8
56	0.039	0.23	0.0
57	0.026	0.15	0.0
58	0.021	0.12	2.9
59	0.022	0.13	0.0
60	0.018	0.10	0.0
61	0.020	0.11	0.0
62	0.029	0.17	0.0
63	0.043	0.25	1.5
64	0.016	0.09	0.0
65	0.010	0.06	5.2
Blank Filter 1	0.016	0.09	0.0
Blank Filter 2	0.009	0.05	0.0
Blank Filter 3	0.019	0.11	0.0
Blank Filter 4	0.019	0.11	0.0

GRAPH 5.7 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF COPPER

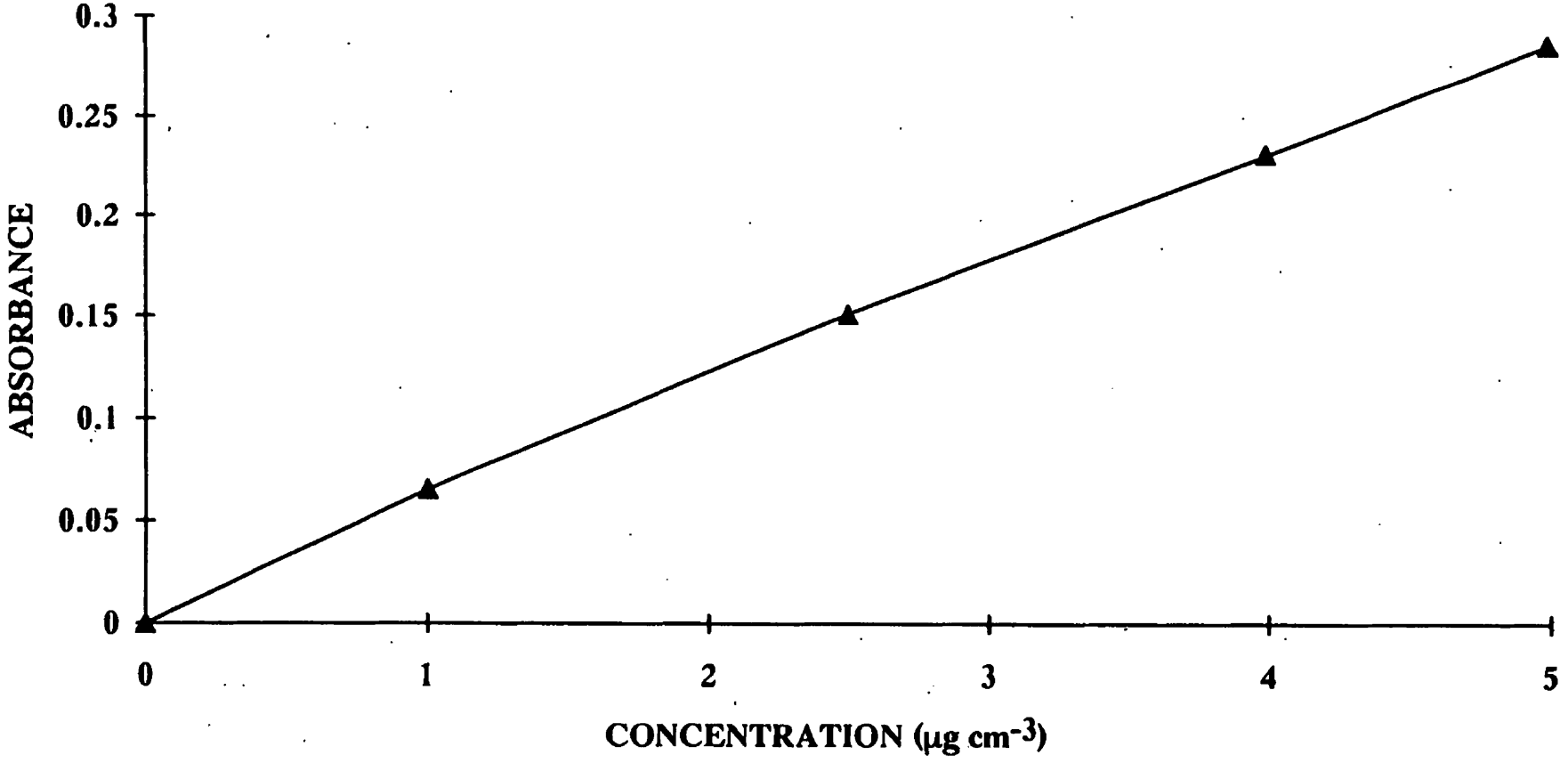


TABLE 5.8 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF IRON**

Flame : Acetylene/Air
Wavelength : 248.3 nm

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.000		
STD 1	0.092	1.00	0.7
STD 2	0.187	2.50	0.0
STD 3	0.273	4.00	0.5
STD 4	0.323	5.00	0.4
4	0.032	0.31	3.7
5	0.040	0.39	1.5
6	0.068	0.70	1.9
7	0.023	0.22	2.4
8	0.036	0.35	0.0
9	0.033	0.32	1.8
10	0.024	0.22	0.0
11	0.046	0.45	0.0
12	0.054	0.54	0.0
14	0.017	0.16	0.0
15	0.040	0.39	1.5
16	0.024	0.22	0.0
17	0.017	0.16	0.0
18	0.045	0.44	0.0
19	0.103	1.14	0.0
20	0.026	0.24	0.0
21	0.027	0.26	2.1
22	0.030	0.29	1.9
23	0.032	0.31	1.8
24	0.031	0.30	1.9
25	0.025	0.23	0.0
26	0.000	0.00	0.0
27	0.034	0.33	1.7
28	0.007	0.07	5.2
29	0.003	0.03	0.0
30	0.000	0.00	0.0
31	0.003	0.03	0.0
32	0.015	0.14	3.3
33	0.113	1.28	0.6
Blank Filter 1	0.002	0.01	0.0
Blank Filter 2	0.011	0.11	0.0

TABLE 5.8 CONTINUED ...

Sample No	ABS	CONC (μg cm^{-3})	RSD %
STD 1	0.035	1.00	1.5
STD 2	0.077	2.50	0.8
STD 3	0.188	4.00	1.1
STD 4	0.143	5.00	1.4
34	0.084	2.71	0.7
35	0.092	3.02	0.0
36	0.123	4.20	2.1
37	0.050	1.46	1.1
38	0.057	1.70	3.1
39	0.069	2.14	0.9
40	0.089	2.89	0.7
41	0.103	3.43	1.2
42	0.123	4.18	0.5
43	0.100	3.31	0.0
44	0.109	3.65	0.0
45	0.137	4.77	0.0
46	0.040	1.14	2.7
47	0.045	1.31	0.0
48	0.047	1.37	0.0
49	0.055	1.63	1.0
50	0.065	2.01	1.8
51	0.059	1.79	0.0
52	0.058	1.73	1.0
53	0.077	2.50	0.8
54	0.230	9.20	0.3
55	0.332	15.95	1.0
56	0.318	14.90	0.9
57	0.069	2.14	0.9
58	0.072	2.28	0.0
59	0.099	3.26	0.6
60	0.039	1.09	4.1
61	0.046	1.32	1.2
62	0.086	2.82	0.7
63	0.091	3.00	0.7
64	0.117	3.96	2.2
Blank Filter 1	0.016	0.43	0.0
Blank Filter 2	0.019	0.51	4.4
Blank Filter 3	0.020	0.52	2.2
FBlank ilter 4	0.018	0.48	4.6

GRAPH 5.8 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF IRON

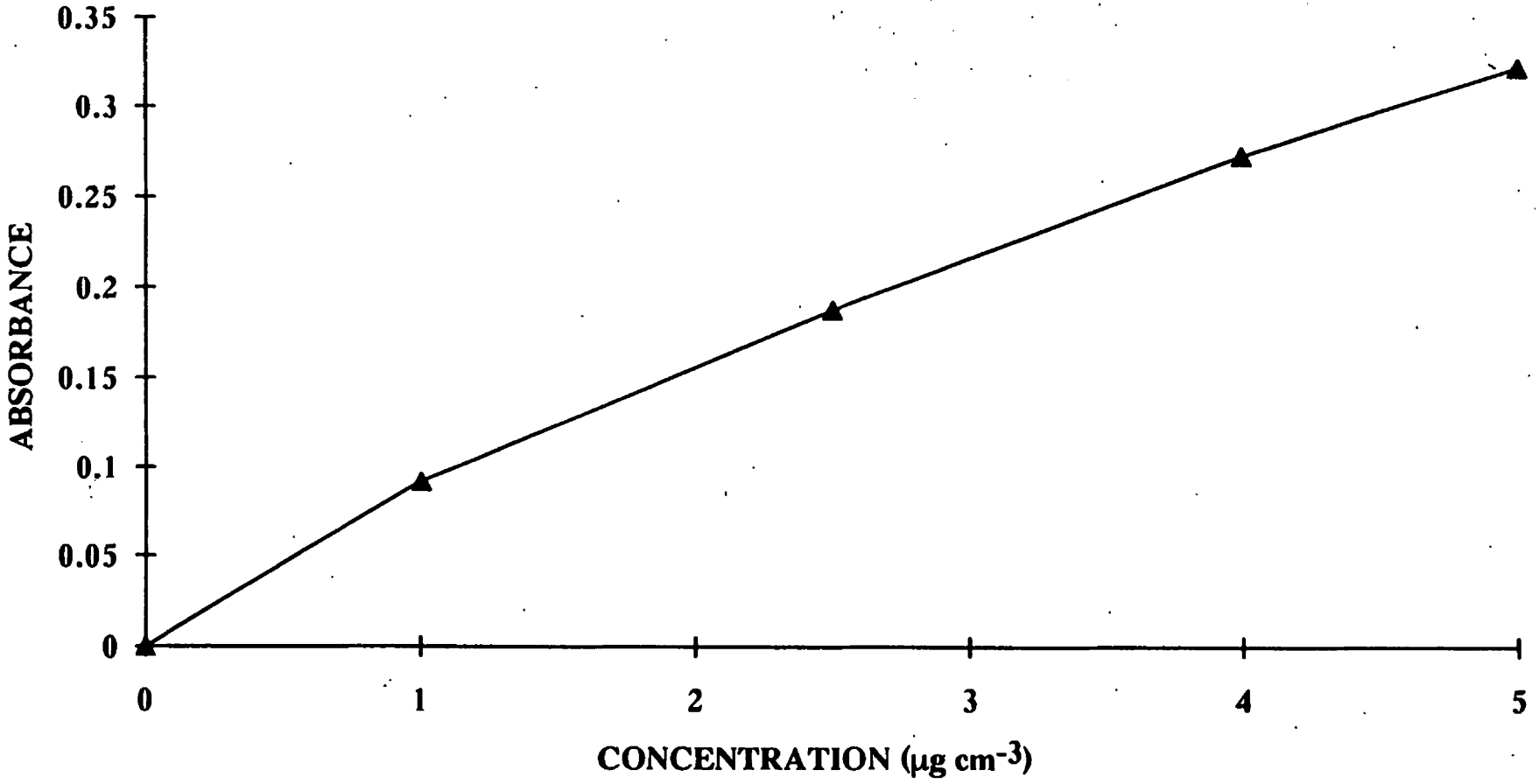


TABLE 5.9 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF LEAD**

Flame : Acetylene/Air
Wavelength : 217.0 nm

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.00		
STD 1	0.054	1.00	2.2
STD 2	0.124	2.50	0.0
STD 3	0.199	4.00	0.6
STD 4	0.245	5.00	0.2
1	0.002	0.03	7.9
2	0.006	0.10	1.8
4	0.007	0.12	0.0
5	0.009	0.16	0.0
6	0.006	0.10	0.0
7	0.008	0.13	1.7
8	0.010	0.17	0.0
9	0.005	0.09	0.0
10	0.008	0.14	3.4
11	0.008	0.14	0.0
12	0.008	0.14	0.0
14	0.003	0.04	1.6
15	0.004	0.07	0.0
16	0.005	0.08	1.5
17	0.004	0.07	0.0
18	0.003	0.05	0.0
19	0.005	0.08	1.5
20	0.001	0.02	0.0
21	0.003	0.04	0.0
22	0.003	0.05	5.7
23	0.003	0.05	5.7
24	0.001	0.01	0.0
25	0.003	0.05	5.7
26	0.000	0.00	9.4
27	0.000	0.00	7.4
28	0.000	0.00	8.3
29	0.001	0.02	6.7
30	0.000	0.00	9.4
9	0.001	0.02	6.7
32	0.006	0.10	9.4
33	0.008	0.14	4.0
Blank Filter 1	0.001	0.02	6.7
Blank Filter	0.007	0.12	0.0

TABLE 5.9 CONTINUED ...

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.000		
STD 1	0.064	1.00	0.9
STD 2	0.163	2.50	0.0
STD 3	0.246	4.00	1.1
STD 4	0.310	5.00	0.2
34	0.007	0.10	6.4
35	0.005	0.08	3.4
36	0.012	0.18	0.0
37	0.006	0.10	0.0
38	0.007	0.10	6.4
39	0.012	0.18	0.0
40	0.011	0.17	5.4
41	0.010	0.15	5.7
42	0.016	0.24	0.0
43	0.025	0.39	1.7
44	0.025	0.40	0.0
45	0.038	0.60	1.3
36	0.003	0.05	3.8
47	0.003	0.06	0.0
48	0.006	0.09	3.3
49	0.009	0.14	2.9
50	0.011	0.17	2.7
51	0.007	0.11	3.1
52	0.008	0.13	5.9
53	0.012	0.20	0.0
54	0.065	1.02	1.7
55	0.079	1.23	0.7
56	0.116	1.79	1.1
57	0.010	0.17	0.0
58	0.011	0.17	5.4
59	0.017	0.27	6.5
60	0.007	0.10	6.4
61	0.008	0.13	0.0
62	0.016	0.26	4.4
63	0.016	0.25	2.2
64	0.022	0.35	1.9
69*	1.519	20.60	0.5
70*	0.020	0.31	6.0
71*	0.037	0.58	1.3
74*	0.032	0.49	3.0
75*	0.014	0.22	2.4

TABLE 5.9 CONTINUED ...

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank Filter 1	0.004	0.06	3.6
Blank Filter 2	0.007	0.11	15.7
Blank Filter 3	0.004	0.07	0.0
Blank Filter 4	0.006	0.10	0.0

* Samples from control experiment

GRAPH 5.9 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF LEAD

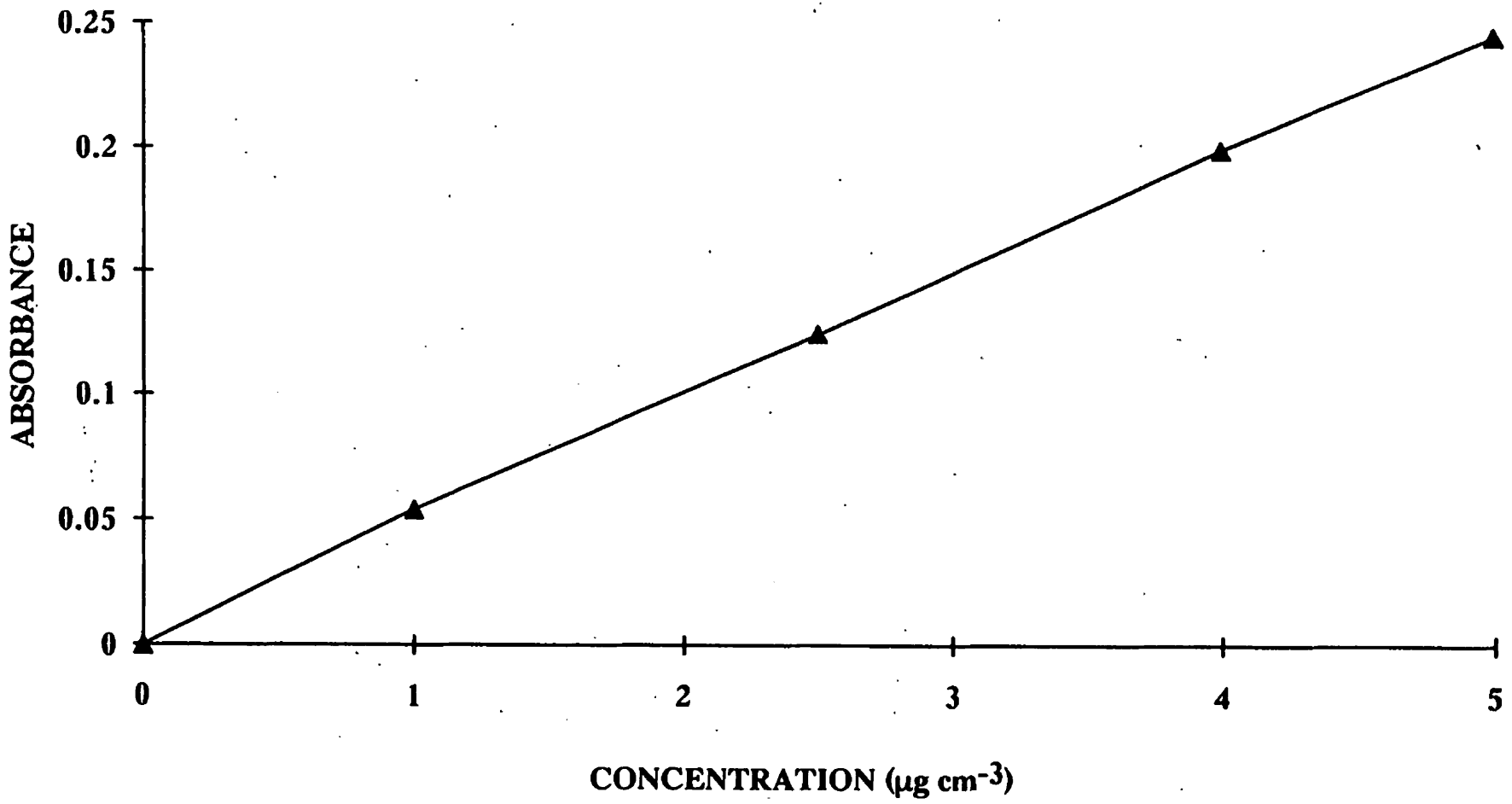


TABLE 5.10 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF NICKEL**

Flame : Acetylene/Air
Wavelength : 232.0 nm

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.000		
STD 1	0.002	1.00	8.3
STD 2	0.006	2.50	5.7
STD 3	0.011	4.00	0.0
STD 4	0.013	5.00	0.0
1	0.001	0.27	0.0
2	0.000	0.00	10.9
4	0.001	0.00	10.0
5	0.001	0.27	9.4
6	0.000	0.53	0.0
7	0.000	0.00	0.0
8	0.001	0.27	0.0
9	0.00	0.00	0.0
10	0.001	0.27	0.0
11	0.003	0.83	12.9
12	0.002	0.66	0.0
14	0.002	1.00	15.7
15	0.002	0.49	0.0
16	0.003	0.66	0.0
17	0.003	1.00	12.9
18	0.002	0.83	0.0
19	0.002	0.66	0.0
20	0.002	0.66	0.0
21	0.002	0.54	15.7
22	0.002	0.40	0.0
23	0.002	0.40	0.0
24	0.001	0.13	0.0
25	0.003	0.69	0.0
26	0.002	0.40	0.0
27	0.002	0.40	0.0
28	0.001	0.13	0.0
29	0.002	0.40	0.0
30	0.001	0.26	20.2
31	0.003	0.69	0.0
32	0.003	0.69	0.0
33	0.003	0.84	12.9
Blank Filter 1	0.003	1.00	0.0
Blank Filter 2	0.000	0.00	10.9

GRAPH 5.10 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF NICKEL

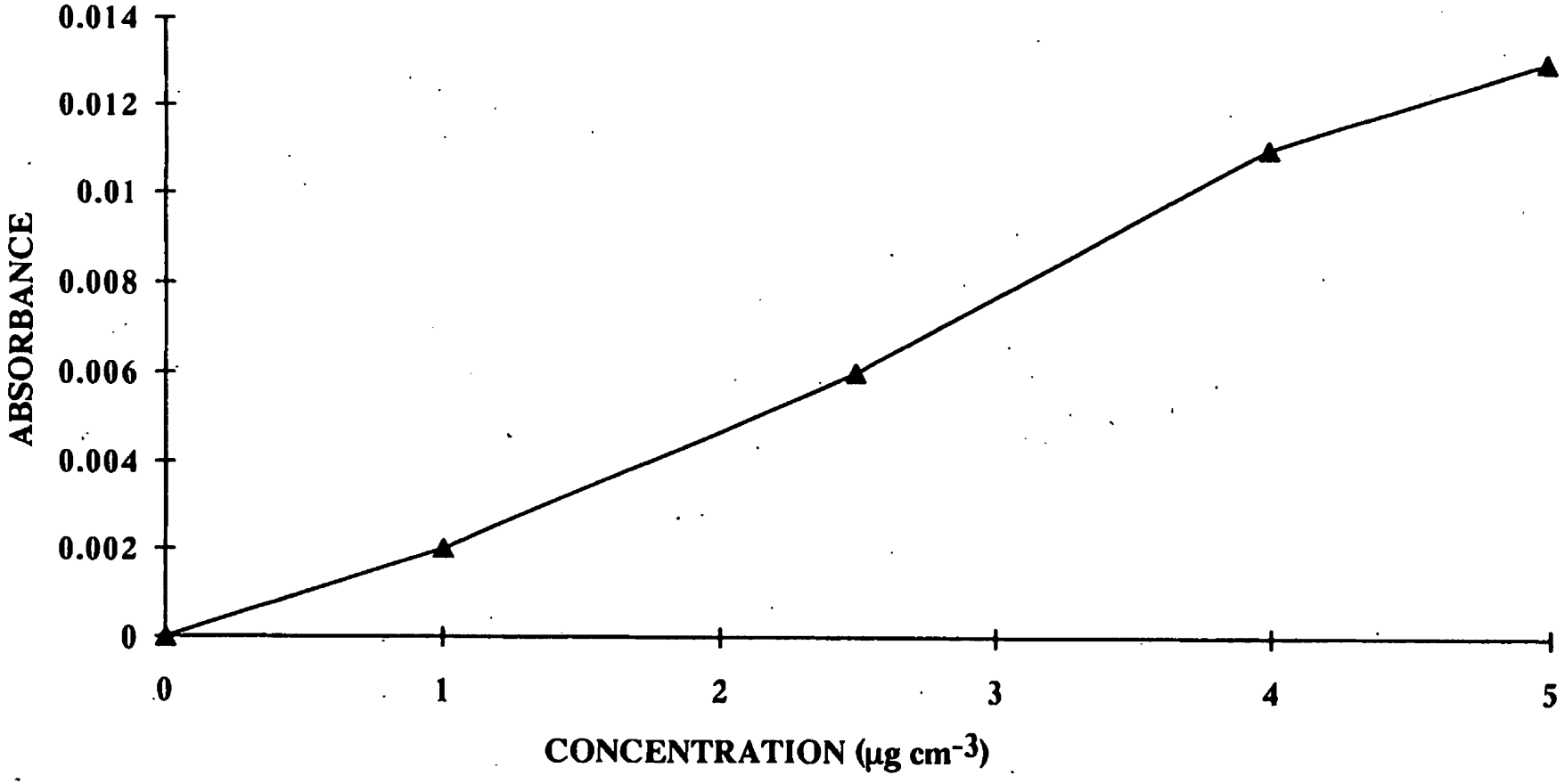


TABLE 5.11 **CALIBRATION CURVE and SAMPLE ANALYSIS RESULTS FOR THE ATOMIC ABSORPTION DETERMINATION OF ZINC**

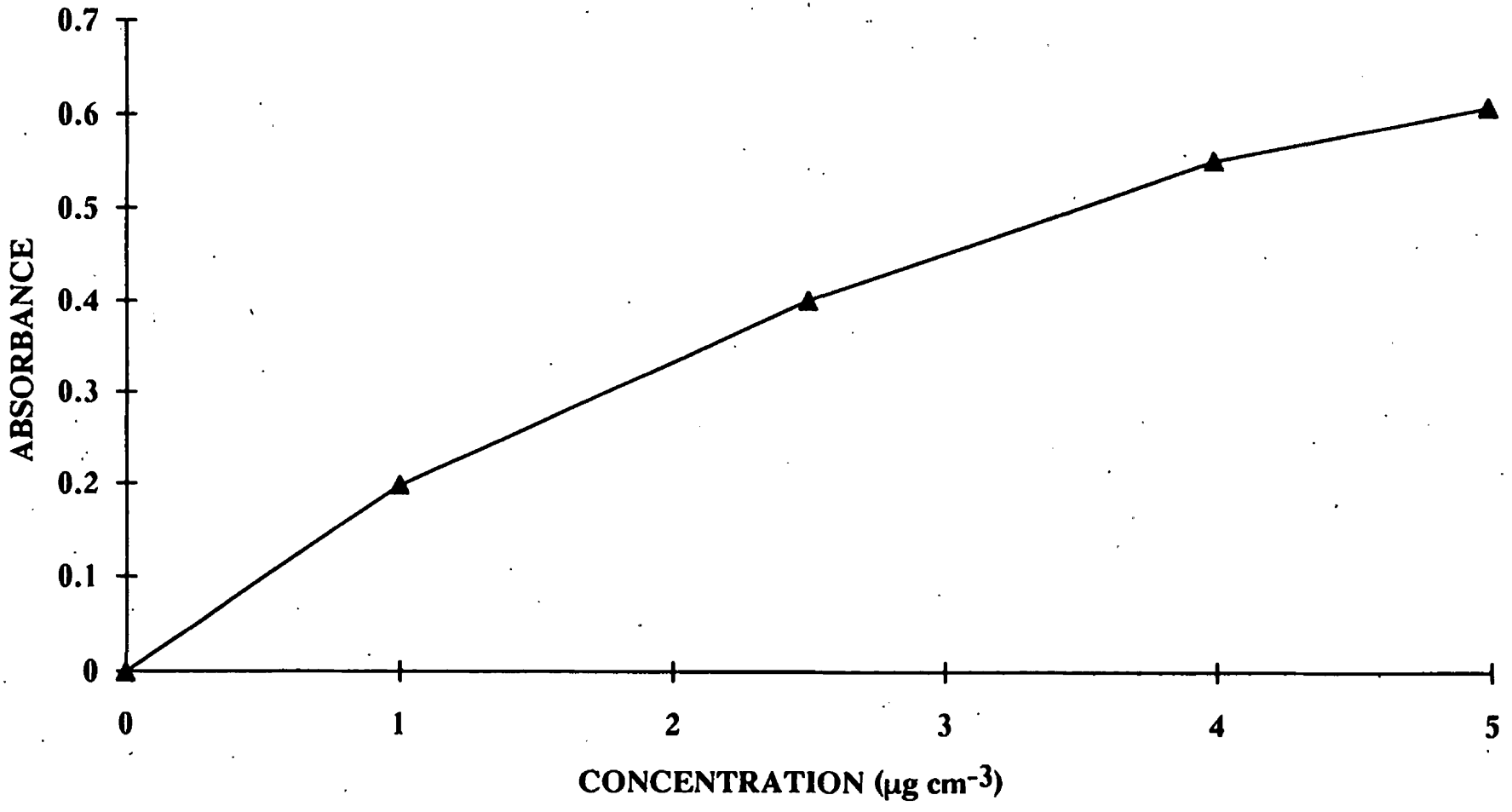
Flame : Acetylene/Air
Wavelength : 213.9 nm

Sample No.	ABS	CONC ($\mu g\ cm^{-3}$)	RSD %
Blank	0.000		
STD 1	0.198	1.00	0.3
STD 2	0.401	2.50	0.5
STD 3	0.551	4.00	0.3
STD 4	0.609	5.00	0.0
9	0.048	0.21	2.4
11	0.036	0.16	4.5
14	0.020	0.09	2.2
15	0.021	0.09	2.2
16	0.022	0.10	2.1
17	0.019	0.08	4.7
18	0.031	0.13	6.7
19	0.038	0.16	0.0
20	0.014	0.06	2.8
24	0.017	0.07	0.0
25	0.017	0.07	2.5
27	0.021	0.09	0.0
28	0.005	0.02	0.0
29	0.007	0.03	3.8
30	0.005	0.02	0.0
31	0.002	0.01	0.0
32	0.017	0.07	0.0
33	0.010	0.04	6.7
Blank Filter	0.000	0.00	6.7

TABLE 5.11 CONTINUED ...

Sample No.	ABS	CONC (μg cm^{-3})	RSD %
Blank	0.000		
STD 1	0.333	1.00	1.0
STD 2	0.583	2.50	0.1
STD 3	0.734	4.00	0.1
STD 4	0.799	5.00	0.1
34	0.143	0.35	0.5
35	0.113	0.27	1.2
36	0.134	0.32	1.5
37	0.134	0.32	0.5
38	0.141	0.34	0.0
39	0.166	0.42	1.2
40	0.212	0.55	0.6
41	0.214	0.56	0.3
42	0.268	0.75	0.3
43	0.235	0.63	0.3
44	0.249	0.68	2.5
45	0.308	0.90	0.4
46	0.114	0.27	0.0
47	0.120	0.29	2.8
48	0.138	0.33	0.0
49	0.146	0.36	0.5
50	0.166	0.42	0.4
51	0.191	0.49	1.8
52	0.186	0.47	0.4
53	0.240	0.65	1.4
54	0.438	1.50	0.5
55	0.484	1.77	0.7
56	0.591	2.56	0.0
57	0.139	0.34	0.0
58	0.139	0.34	0.5
59	0.170	0.43	1.2
60	0.113	0.27	0.0
61	0.118	0.28	0.0
62	0.144	0.35	1.9
63	0.148	0.36	1.8
64	0.166	0.42	2.0
Blank Filter 1	0.084	0.19	3.8
Blank Filter 2	0.080	0.18	0.0
Blank Filter 3	0.081	0.19	2.4
Blank Filter 4	0.082	0.19	1.6

GRAPH 5.11 - CALIBRATION GRAPH FOR THE ATOMIC ABSORPTION OF ZINC



CHAPTER SIX

DISCUSSION

6.1 Interpretation of analyses from emission air sampling data

When the results from the first survey had been evaluated, it was clear that amounts of metal pollutant were close to or even below the limits of sensitivity of the atomic absorption spectrometer. In the cases of aluminium and nickel, the absorbances for their standard solutions were too low to provide an accurate calibration graph and no further attempt was made to determine their concentrations in the air sample.

In the cases of cadmium, chromium and cobalt, absorbances obtained from the analysis of blank filter papers were broadly similar to the absorbances obtained from the sample filter papers. These made results for these metals unreliable and are therefore reported as none detected.

Positive results are reported for copper, iron, lead and zinc. However, for the analytical equipment used in this project, the manufacturer states that only results greater than 0.1 ppm (ie. 100 ng m^{-3}) can be deemed reliable. Scrutiny of results quoted in this project show only iron producing quantities above the stated minimum. However, all positive results are reported and it is interesting to note that they broadly agree with the multi-element statistical survey carried out by Warren Spring Laboratory in the UK between 1976-1989 **[21]**.

If the results are studied for iron in particular, the results from the FC emission points and the control point are similar in any one sampling run. This would suggest that background levels are being monitored with no extra contribution from the FC emission points. Indeed, in some cases results are higher at the control point than at the emission ductings. This could possibly be explained

by the control points near proximity to an emission stack from a boiler responsible for the building's heating.

The above observations also relate to the results for copper, lead and zinc, although because of low levels the results tend to be unreliable.

Although the relative standard deviations (RSD%) of the absorbance measurements were recorded in each table of results, no significant importance was attached to these figures especially where absorbance readings are extremely low (i.e. less than 0·01 absorbance units).

6.2 Interpretation of analyses from the controlled air sampling data

Large amounts of metal polluted air were generated artificially in a fume cupboard by atomisation of concentrated "metal" solutions (Cr and Pb). This air was collected within the fume cupboard and also at its emission point. The object of these measurements was to estimate the efficiency of ventilation of the metal ions generated.

As expected, collection of air within the fume cupboard produced large amounts of the atomised metal on analysis of the filter. Simultaneous measurements at the emission point produced amounts less than 5% of that collected inside. At this stage it was assumed the efficiency of the interior collection accounted for the low figures obtained at the emission points.

However, when the experiments were repeated with collections only taking place at the roof emission points, again only small amounts of metal pollutant were collected on the filters. Knowing large amounts were still being generated via the atomic absorption atomiser, the question arose as to where

the majority of these metal ions were ending up. With the fume cupboard fan drawing the air through the ducting, it is assumed that the majority of the metal ions produced are depositing on the wall of the ducting and not emerging onto the roof.

6.3 Discussion on the optimisation of air sampling criteria

Once the sampling apparatus was assembled and fully tested for efficiency of air collection and volume measurement, the question arose as to what parameters should be applied to the sampling run. These parameters included :

- air sampling rate (litres/min)
- sampling time (hours/days/months)
- continuous or intermittent air collection during designated time period

Careful consideration was given to the objectives of the study before setting up the above parameters.

One of the original objectives of this project was to relate incidents in the Science laboratories to any metal pollutant found emitted during the sampling run. For this reason a time period of 24 hours was initially chosen, starting 9-10.00 am and running through until the following morning. This was envisaged to be the minimum time for collection due to the small amounts of particulate matter expected. Even then the emission ductings would not be in use a large proportion of this 24 hours period during the day and obviously not at all during the night. To try and offset this the pump rates were set at their maximum, which in these systems were 13-15 litres/min. Therefore, during the first survey total volumes of air collected were in the region of 16-20,000 litres.

The extremely low results from the above survey prompted a re-think for setting the parameters of the second survey. As the pumps were already running at a maximum, sampling times were increased to collect larger amounts of particulate matter and perhaps measurable amounts of metal pollutant. Even when up to ten times the volume of air was collected, measured metal pollutant levels were near the detection limit of the atomic absorption spectrometer. As these levels very rarely exceeded background levels given by the controlled monitoring stations, no relationship between laboratory activity and levels of metal pollutant measured could be established.

Any future projects undertaken in order to relate the laboratory emissions to metal pollutants should look at methods of stopping air collection during inactive periods of time, and starting again when fume cupboard ventilation is in use.

CHAPTER SEVEN

CONCLUSIONS and RECOMMENDATIONS

7.1 Conclusions

It was recognised from the first survey results that extremely low concentrations of trace metals were being collected (most were below the analytical detection limit of the atomic absorption spectrometer). Even when sampling times were increased in the second survey, only results for four metals can be considered to be reliable ie. Iron, Copper, Lead and Zinc.

However, both surveys show that there is no significant emission of trace metal pollutants from the Institute laboratories and thus no significant environmental burden on the surrounding area. In fact none of the measurements would appear to indicate anything more than background levels being monitored. The observed differences between sampling runs are probably due to meteorological influences such as wind speed and direction or overcast cloud.

An established procedure has been laid down for the digestion of the filter paper and particulates collected resulting in homogenous solutions that are required for analysis by atomic absorption spectrophotometry.

Following the low results encountered from the rooftop surveys, it could be concluded that measurement by atomic absorption spectrophotometry is too insensitive for this design of experiment, and other methods of analysis would need to be considered. If this is the case, methods measuring down to parts per billion would be more appropriate.

Alternatively if sampling runs were carried out for a longer period of time, larger amounts of particulate matter would be collected producing greater amounts of metal pollutant and more in the range of the atomic absorption

spectrometer. This, however, would make it impractical to relate unusually high levels to incidents within the laboratory and thus the objectives of such a study would not be realised.

Results from the controlled air sampling experiment proved more revealing. It would seem that the extraction of the fume cupboard does not effectively ventilate the generated metal polluted air from within the cupboard, and that the ducting leading to the roof acts as a condenser for the metal ions drawn into it. If this were true then rooftop collection measurements would never reflect the amounts of pollutant produced in the laboratories. Although this would seem to reduce the risk of any environmental burden to the area surrounding the Institute, it would be highly desirable to understand what actually happens to the trace metal pollutants that may be generated. Further experiments need to be carried out to answer this question and recommendations are put forward later in this chapter.

Despite the difficulties encountered looking for trends in measurements at such low levels, several objectives have been achieved during this study.

- The successful setting up of several air monitoring stations with emphasis on portability and ability to withstand adverse weather conditions. This monitoring system is adaptable in that it can be quickly set up at any site and different collection mediums can be substituted to allow for different air pollutants to be measured.
- A successful procedure for preparation of the sample for atomic absorption measurements has been established for comparison with standard metal solutions.

- The results from two rooftop surveys carried out over a three month period show no significant environmental burden on urban areas surrounding the Institute.

7.2 Recommendations

From the discussion and subsequent conclusions drawn, the following recommendations are put forward :

- **Increase sampling times in order to collect larger amounts of particulate matter.** This, in turn, would realise greater amounts of the measured pollutant and hence fall within the analytical detection limits of the atomic absorption spectrometer. Alternatively, larger more powerful pumps could be substituted to increase sampling rates without increasing sampling times. This, however, would involve greater expense and, in all probability, decrease the portability of the air collection system.

- **Investigate more sensitive methods of analysis.** However, availability of such equipment may prove a problem and can often involve complex preparation techniques. Methods that fall into this category include :

  Graphite furnace atomic absorption spectrophotometry (GF-AAS)
  Inductively coupled plasma emission spectrophotometry (ICP-ES)
  Inductively coupled plasma mass spectrometry (ICP-MS)
  Atomic fluorescence spectrometry (AFS)

- **Outside air collection measurements should be accompanied by meteorological measurements sited at the monitoring stations.** This could account for variations in background levels. Wind speed and direction, temperature and humidity measurements may explain these variations. In some instances, wind direction measurement could pinpoint the source of pollutant emission.

- **Further controlled experiments to take place within the confines of the fume cupboard and ducting.** Air collection using probes inserted at varying distances along the ducting should provide data on possible condensation of trace metal ions.
- **Increase the number of control sampling stations.** This would record background levels more accurately and negate any contributions from close proximity of emission stacks.

- **Further surveys could be carried out at the FC emission points with air collection only taking place while fume cupboard ventilation was taken place.** This could be done by fitting an ON/OFF switch between the fume cupboard fan and the pumps set on manual mode.

Some problems were encountered during the setting up and running of the air collection system and subsequent analysis of the air collection mediums. These form the basis of the recommendations above, and together with data accumulated during this study could possibly provide starting points for future projects to be undertaken.

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REFERENCES

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